

Supporting information for the article entitled

Iridium-Catalyzed Alkenyl C-H Allylation Using Conjugated Dienes

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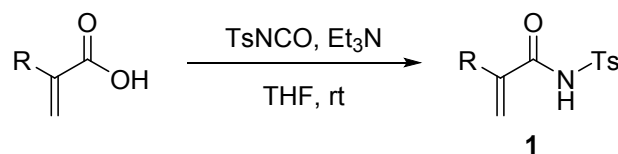
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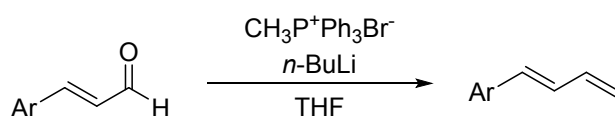
General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on Bruker AMX 400 spectrophotometer (CDCl_3 as solvent), and Bruker AMX 500 spectrophotometer (CDCl_3 as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-ToF Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). $[\text{IrOMe}(\text{cod})]_2$ was purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification.

Substrate Synthesis

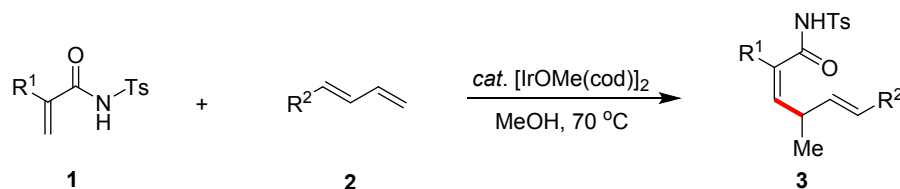


To a solution of α -substituted acrylic acid (1.0 mmol, 1.0 equiv) in dry THF (2 mL, 0.5 M) was added *p*-tosyl isocyanate (1.0 mmol, 1.0 equiv). After stirring the resulting clear solution at r.t. for 10 min, triethyl amine (1.0 mmol, 1.0 equiv) was added in dropwise, with release of gas. The progress of the reaction was monitored using TLC. Once the acrylic acids disappeared, the mixture was diluted with EtOAc and washed with 2 M HCl. The organic layer was dried over MgSO_4 , filtered and concentrated in vacuo. The residue was subjected to column chromatography on silica gel to deliver acrylamide **1**.¹



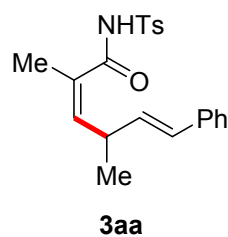
To a suspension of methyltriphenylphosphonium bromide (6.0 mmol) in dry THF (30 mL) was added *n*-BuLi (2.3 mL: 2.6 M in *n*-hexane, 3.6 mmol) at 0 °C under argon. After stirring for 40 min, a cinnamaldehyde derivative (6.0 mmol) was added. The reaction mixture was warmed to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with Sat. NH_4Cl (aqueous, 10 mL) and extracted with EtOAc (10 mL \times 2). The combined organic layers were dried over MgSO_4 , and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1-aryl-1,3-butadiene derivative.

General Procedure for the Cross-Coupling between Acrylamides and Butadienes



A dry screw-cap vial was charged with [IrOMe(cod)]₂ (5 mol%, 0.01 mmol) and methanol (1.0 mL). Then, acrylamide **1** (1.0 equiv, 0.2 mmol) and butadiene **2** (1.2 equiv, 0.24 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 70 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography for separation (ethyl acetate/petroleum ether mixtures) to provide 1,4-diene product **3**.

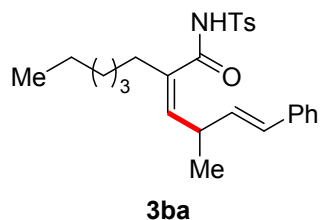
Characterization Data



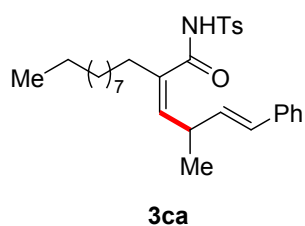
(2Z, 5E)-2, 4-dimethyl-6-phenyl-N-tosylhexa-2, 5-dienamide

(3aa): Following the general procedure, **3aa** was obtained as a yellow liquid, yield = 90%. ¹H NMR (500 MHz, CDCl₃): δ = 1.13 (d, *J* = 6.5 Hz, 3H), 1.87 (d, *J* = 1.5 Hz, 3H), 2.42 (s, 3H), 3.56-

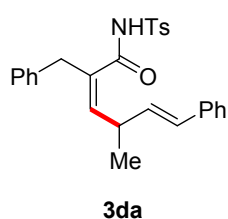
3.48 (m, 1H), 5.64 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.05 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 7.21 (tt, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.34-7.27 (m, 6H), 7.95-7.99 (d, *J* = 8.5 Hz, 2H), 8.43 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.24, 19.86, 20.66, 36.00, 125.20, 126.37, 126.99, 127.45, 127.49, 128.40, 128.57, 131.75, 134.61, 135.99, 141.46, 144.09, 165.01. HRMS (ESI): *m/z* for C₂₁H₂₄NO₃S [M+H]⁺: 370.1471, found: 370.1473. FTIR (KBr, cm⁻¹): 3251.40, 2962.62, 2923.36, 1698.13, 1417.13, 1169.29, 1078.50, 666.36.



(Z)-2-((E)-2-methyl-4-phenylbut-3-en-1-ylidene)-N-tosyl-octanamide (3ba): Following the general procedure, **3ba** was obtained as a white liquid, yield = 89%. ¹H NMR (500 MHz, CDCl₃): δ = 0.84 (t, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.26-1.15 (m, 8H), 2.22-2.09 (m, 2H), 2.42 (s, 3H), 3.35-3.28 (m, 1H), 5.52 (d, *J* = 10.0 Hz, 1H), 6.06 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.35 (d, *J* = 15.5 Hz, 1H), 7.21 (tt, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.35-7.28 (m, 6H), 7.97 (d, *J* = 8.5 Hz, 2H), 8.42 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 13.01, 20.05, 20.65, 21.42, 27.04, 27.56, 30.41, 33.29, 36.18, 125.22, 126.39, 127.40, 127.50, 128.31, 128.53, 131.89, 133.09, 134.57, 135.94, 137.74, 144.08, 165.67. HRMS (ESI): *m/z* for C₂₆H₃₄NO₃S [M+H]⁺: 440.2254, found: 440.2256. FTIR (KBr, cm⁻¹): 3473.20. 3416.28. 2926.17. 1614.02. 1400.93. 1162.62. 1081.31.

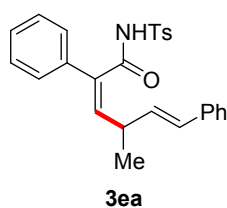


(Z)-2-((E)-2-methyl-4-phenylbut-3-en-1-ylidene)-N-tosyl-dodecanamide (3ca): Following the general procedure, **3ca** was obtained as a white liquid, yield = 88%. ¹H NMR (500 MHz, CDCl₃): δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 7.0 Hz, 3H), 1.29-1.18 (m, 16H), 2.23-2.08 (m, 2H), 2.43 (s, 3H), 3.36-3.28 (m, 1H), 5.53 (d, *J* = 10.5 Hz, 1H), 6.06 (dd, *J* = 16.0 Hz, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 7.22 (tt, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.36-7.29 (m, 6H), 7.97 (d, *J* = 8.5 Hz, 2H), 8.27 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 13.10, 20.13, 20.67, 21.66, 27.13, 27.96, 28.26, 28.28, 28.46, 28.55, 30.87, 33.31, 36.27, 125.23, 126.44, 127.43, 127.53, 128.40, 128.54, 131.86, 133.14, 134.58, 135.90, 137.75, 144.08, 165.56. HRMS (ESI): *m/z* for C₃₀H₄₂NO₃S [M+H]⁺: 496.2880, found: 496.2883. FTIR (KBr, cm⁻¹): 3550.32, 3415.66, 2923.36, 1615.56, 1398.13.



(2Z, 5E)-2-benzyl-4-methyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3da): Following the general procedure, **3da** was obtained as a white solid, m.p.: 168.1 °C, yield = 74%. ¹H NMR (500 MHz,

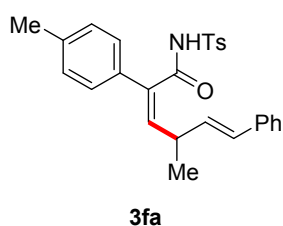
CDCl₃): δ = 1.18 (d, J = 6.5 Hz, 3H), 2.42 (s, 3H), 3.54-3.44 (m, 3H), 5.66 (d, J = 10.5 Hz, 1H), 6.09 (dd, J = 15.5 Hz, J = 7.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 7.03-7.01 (m, 2H), 7.25-7.20 (m, 6H), 7.36-7.29 (m, 4H), 7.74 (d, J = 8.5 Hz, 2H), 8.00 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 20.02, 20.66, 36.27, 39.46, 125.26, 125.88, 126.47, 127.29, 127.45, 127.53, 127.88, 128.44, 128.64, 131.52, 131.70, 134.29, 135.88, 136.30, 140.53, 143.85, 164.72. HRMS (ESI): m/z for C₂₇H₂₈NO₃S [M+H]⁺: 446.1784, found: 446.1787. FTIR (KBr, cm⁻¹): 3450.59, 2962.75, 1647.81, 1402.96, 1260.90, 810.09.



(2Z, 5E)-4-methyl-2, 6-diphenyl-N-tosylhexa-2, 5-dienamide

(3ea): Following the general procedure, **3ea** was obtained as a white solid, m.p.: 110.3 °C, yield = 80%. ¹H NMR (500 MHz, CDCl₃): δ = 1.21 (d, J = 6.5 Hz, 3H), 2.45 (s, 3H), 3.62-3.55 (m,

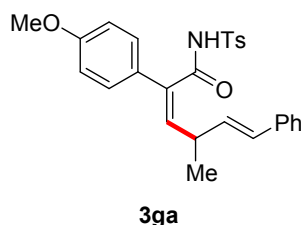
1H), 5.99 (d, J = 10.0 Hz, 1H), 6.10 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H), 6.34 (d, J = 15.5 Hz, 1H), 7.15-7.13 (m, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.35-7.26 (m, 9H), 7.94 (d, J = 8.0 Hz, 2H), 8.18 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.51, 20.68, 36.11, 125.17, 126.09, 126.31, 127.46, 127.47, 127.62, 127.95, 128.55, 131.34, 132.90, 134.51, 134.72, 136.13, 141.55, 144.15, 164.17. HRMS (ESI): m/z for C₂₆H₂₆NO₃S [M+H]⁺: 432.1628, found: 432.1634. FTIR (KBr, cm⁻¹): 3473.23, 3416.00, 2920.56, 1616.82, 1406.54.



(2Z, 5E)-4-methyl-6-phenyl-2-(p-tolyl)-N-tosylhexa-2, 5-dienamide (3fa): Following the general procedure, **3fa** was

obtained as a white solid, m.p.: 135.4 °C, yield = 71%. ¹H NMR (500 MHz, CDCl₃): δ = 1.21 (d, J = 7.0 Hz, 3H), 2.34 (s, 3H), 2.46 (s, 3H), 3.67-3.60 (m, 1H), 5.96 (d, J = 10.5 Hz, 1H), 6.10 (dd, J = 16.0 Hz, J = 6.5 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 7.03 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 7.0 Hz, 1H), 7.33-7.27 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.98 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.55, 20.12, 20.71, 36.02, 125.15, 126.16, 126.29, 127.47, 128.44, 128.56, 128.68, 131.48, 131.96,

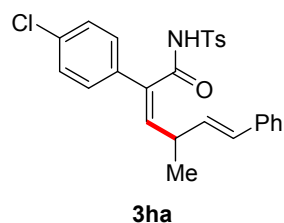
132.54, 134.52, 136.15, 137.73, 141.71, 144.13, 164.12. HRMS (ESI): m/z for $C_{27}H_{28}NO_3S$ $[M+H]^+$: 446.1784, found: 446.1776. FTIR (KBr, cm^{-1}): 3444.86, 2923.36, 1658.88, 1647.66, 1400.93.



(2Z,5E)-2-(4-methoxyphenyl)-4-methyl-6-phenyl-N-

tosylhexa-2,5-dienamide (3ga): Following the general procedure, **3ga** was obtained as a yellow liquid, yield = 50%.

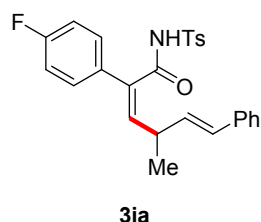
1H NMR (500 MHz, $CDCl_3$): δ = 1.21 (d, J = 7.0 Hz, 3H), 2.47 (s, 3H), 3.65-3.58 (m, 1H), 3.81 (s, 3H), 5.92 (d, J = 10.5 Hz, 1H), 6.10 (dd, J = 15.5 Hz, J = 6.5 Hz, 1H), 6.34 (d, J = 15.5 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 7.08 (d, J = 9.0 Hz, 2H), 7.21 (t, J = 7.0 Hz, 1H), 7.33-7.27 (m, 5H), 7.37 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 19.60, 20.72, 36.04, 54.36, 113.40, 125.15, 126.30, 127.20, 127.47, 127.48, 127.57, 128.38, 128.58, 131.56, 132.19, 134.53, 136.14, 140.90, 144.15, 158.92, 164.22. HRMS (ESI): m/z for $C_{27}H_{28}NO_4S$ $[M+H]^+$: 462.1734, found: 462.1735. FTIR (KBr, cm^{-1}): 3439.25, 2923.36, 2853.27, 1712.15, 1513.08, 1260.15, 1087.80, 1022.43, 812.15.



(2Z,5E)-2-(4-chlorophenyl)-4-methyl-6-phenyl-N-

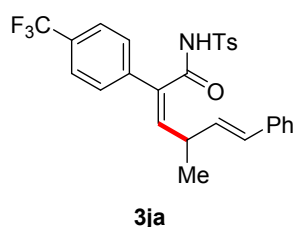
tosylhexa-2, 5-dienamide (3ha): Following the general procedure, **3ha** was obtained as a white solid, m.p.: 168.4 °C, yield = 73%.

1H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, J = 7.0 Hz, 3H), 2.47 (s, 3H), 3.56-3.49 (m, 1H), 5.99 (d, J = 10.5 Hz, 1H), 6.08 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 7.08 (d, J = 8.5 Hz, 2H), 7.22 (t, J = 7.0 Hz, 1H), 7.37-7.26 (m, 8H), 7.94 (d, J = 8.5 Hz, 2H), 8.10 (s, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 19.54, 20.73, 36.34, 125.18, 126.44, 127.25, 127.46, 127.52, 128.14, 128.63, 128.77, 130.97, 131.93, 133.05, 133.71, 134.31, 135.94, 141.44, 144.36, 163.85. HRMS (ESI): m/z for $C_{26}H_{25}ClNO_3S$ $[M+H]^+$: 466.1238, found: 466.1236. FTIR (KBr, cm^{-1}): 3444.71, 2959.95, 2924.55, 1647.81, 1398.28, 1101.08.



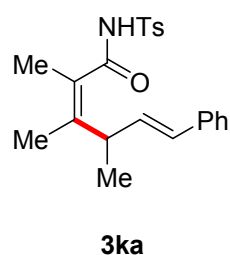
(2Z,5E)-2-(4-fluorophenyl)-4-methyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3ia): Following the general procedure, **3ia** was

obtained as a white solid, m.p.: 143.4 °C, yield = 66%. ¹H NMR (500 MHz, CDCl₃): δ = 1.22 (d, *J* = 6.5 Hz, 3H), 2.47 (s, 3H), 3.58-3.51 (m, 1H), 5.95 (d, *J* = 10.5 Hz, 1H), 6.09 (dd, *J* = 15.5 Hz, *J* = 7.0 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.99 (t, *J* = 8.5 Hz, 2H), 7.14-7.11 (m, 2H), 7.21 (t, *J* = 7.0 Hz, 1H), 7.33-7.28 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 8.08 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.56, 20.72, 36.24, 114.99 (d, *J*_{C-F} = 21.2 Hz), 125.18, 126.41, 127.46, 127.51, 127.91 (d, *J*_{C-F} = 8.8 Hz), 128.61, 128.68, 130.80 (d, *J*_{C-F} = 2.5 Hz), 131.13, 131.90, 134.37, 135.99, 141.41, 144.31, 161.83 (d, *J*_{C-F} = 247.75 Hz), 163.96. HRMS (ESI): *m/z* for C₂₆H₂₅FNO₃S [M+H]⁺: 450.1534, found: 450.1533. FTIR (KBr, cm⁻¹): 3473.05, 2968.22, 2923.36, 2847.66, 1557.94, 1402.87.



(2Z,5E)-4-methyl-6-(trifluoromethyl)phenylhexa-2, 5-dienamide (3ja):

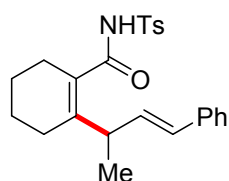
Following the general procedure, **3ja** was obtained as a white solid, m.p.: 173.7 °C, yield = 69%. ¹H NMR (500 MHz, CDCl₃): δ = 1.24 (d, *J* = 6.5 Hz, 3H), 2.47 (s, 3H), 3.56-3.49 (m, 1H), 6.11-6.07 (m, 2H), 6.36 (d, *J* = 15.5 Hz, 1H), 7.22 (tt, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.37-7.26 (m, 8H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 8.5 Hz, 2H), 8.17 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.53, 20.72, 36.53, 122.76 (q, *J*_{C-F} = 270.6 Hz), 124.88 (q, *J*_{C-F} = 7.5 Hz), 125.21, 126.17, 126.53, 127.46, 127.54, 128.65, 129.01, 129.57 (q, *J*_{C-F} = 32.8 Hz), 130.65, 132.01, 134.21, 135.84, 138.01, 142.37, 144.48, 163.66. HRMS (ESI): *m/z* for C₂₇H₂₅F₃NO₃S [M+H]⁺: 500.1502, found: 500.1494. FTIR (KBr, cm⁻¹): 3444.76, 2959.81, 2923.36, 1647.66, 1398.13.



(2Z, 5E)-2, 3, 4-trimethyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3ka):

Following the general procedure, **3ka** was obtained as a white liquid, yield = 58%. ¹H NMR (500 MHz, CDCl₃): δ = 1.12 (d, *J* = 7.0 Hz, 3H), 1.61 (d, *J* = 0.5 Hz, 3H), 1.77 (d, *J* = 1.0 Hz, 3H), 2.42 (s, 3H), 3.40-3.34 (m, 1H), 6.09 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.27 (d, *J* = 16.0 Hz, 1H), 7.22-7.19 (m, 1H), 7.34-7.27 (m, 6H), 7.98

(d, $J = 8.5$ Hz, 2H), 8.30 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 12.57, 14.66, 17.17, 20.66, 39.91, 123.80, 125.16, 126.31, 127.36, 127.49, 128.56, 128.79, 130.97, 134.60, 136.06, 142.67, 144.07, 167.49$. HRMS (ESI): m/z for $\text{C}_{22}\text{H}_{26}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 384.1628, found: 384.1622. FTIR (KBr, cm^{-1}): 3415.98, 2968.22, 2926.17, 1615.44, 1402.51.

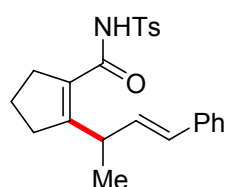


3la

(E)-2-(4-phenylbut-3-en-2-yl)-N-tosylcyclohex-1-ene-1-

carboxamide (3la): Following the general procedure, **3la** was obtained as a white solid, m.p.: 100.3 °C, yield = 88%. ^1H NMR (500 MHz, CDCl_3): $\delta = 1.12$ (d, $J = 7.0$ Hz, 3H), 1.55-1.44 (m,

2H), 1.66-1.59 (m, 2H), 2.22-2.03 (m, 4H), 2.42 (s, 3H), 3.44-.339 (m, 1H), 6.11 (dd, $J = 15.5$ Hz, $J = 6.5$ Hz, 1H), 6.28 (d, $J = 16.0$ Hz, 1H), 7.23-7.19 (m, 1H), 7.34-7.27 (m, 6H), 7.98 (d, $J = 8.0$ Hz, 2H), 8.33 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 17.11, 20.66, 20.84, 23.06, 25.66, 39.25, 125.18, 126.10, 126.30, 127.36, 127.49, 128.54, 128.71, 131.28, 134.65, 136.07, 144.03, 144.41, 167.15$. HRMS (ESI): m/z for $\text{C}_{24}\text{H}_{28}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 410.1784, found: 410.1788. FTIR (KBr, cm^{-1}): 3550.18, 3415.51, 1614.16, 1395.47, 613.24.

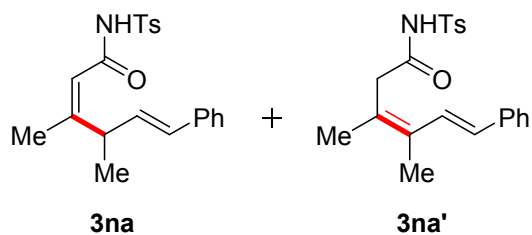


3ma

(E)-2-(4-phenylbut-3-en-2-yl)-N-tosylcyclopent-1-ene-1-

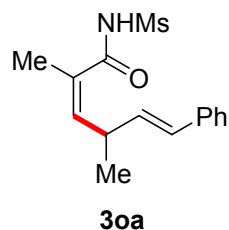
carboxamide (3ma): Following the general procedure, **3ma** was obtained as a light yellow liquid, yield = 89%. ^1H NMR (500 MHz, CDCl_3): $\delta = 1.18$ (d, $J = 7.0$ Hz, 3H), 1.89-1.78 (m, 2H), 2.43 (s,

3H), 2.47-2.49 (m, 4H), 4.36-4.30 (m, 1H), 6.13 (dd, $J = 15.5$ Hz, $J = 7.0$ Hz, 1H), 6.40 (d, $J = 16.0$ Hz, 1H), 7.20 (t, $J = 7.0$ Hz, 1H), 7.34-7.26 (m, 6H), 7.99 (d, $J = 8.5$ Hz, 2H), 8.03 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 17.36, 20.60, 20.66, 32.40, 32.86, 35.29, 125.17, 125.20, 126.25, 127.46, 127.50, 128.52, 128.75, 130.73, 134.91, 136.21, 143.84, 161.50, 163.52$. HRMS (ESI): m/z for $\text{C}_{23}\text{H}_{26}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 396.1628, found: 396.1635. FTIR (KBr, cm^{-1}): 3442.06, 2923.36, 1661.68, 1406.54, 1168.22.



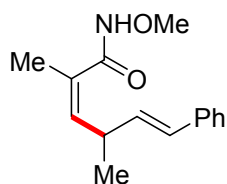
(R, 2Z, 5E)-3, 4-dimethyl-6-phenyl- N-tosylhexa-2, 5-dienamide (3na); (3Z, 5E)-3, 4-dimethyl-6-phenyl-N-tosylhexa-2, 5-dienamide (3na'): Following the general procedure, **3na** and **3na'** was

obtained as a white liquid (**3na** : **3na'** = 1 : 1.8), total yield = 27%. ¹H NMR (500 MHz, CDCl₃) of **3na**: δ = 1.17 (d, *J* = 7.0 Hz, 3H), 1.80 (s, 3H), 2.43 (s, 3H), 4.69-4.62 (m, 1H), 5.56 (s, 1H), 6.11 (dd, *J* = 16.0 Hz, *J* = 6.5 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 7.21-7.18 (m, 1H), 7.34-7.26 (m, 6H), 7.96 (d, *J* = 8.5 Hz, 2H), 8.29 (s, 1H). ¹H NMR (500 MHz, CDCl₃) of **3na'**: δ = 1.86 (s, 5.4H), 1.98 (s, 5.4H), 2.34 (s, 5.4H), 3.29 (s, 3.6H), 6.62 (d, *J* = 16.0 Hz, 1.8H), 6.84 (d, *J* = 16.0 Hz, 1.8H), 7.15 (d, *J* = 8.0 Hz, 3.6H), 7.34-7.26 (m, 9H), 7.83 (d, *J* = 8.5 Hz, 3.6H), 8.29 (s, 1.8H). ¹³C NMR (125 Hz, CDCl₃): δ = 14.01, 16.66, 19.45, 19.98, 20.61, 20.65, 36.45, 41.50, 114.55, 124.79, 125.11, 125.48, 125.52, 126.21, 126.71, 127.28, 127.45, 127.62, 128.52, 128.57, 129.06, 129.26, 130.54, 132.05, 134.14, 134.95, 136.22, 136.25, 143.83, 144.02, 161.50, 164.61, 167.50. HRMS (ESI): *m/z* for C₂₁H₂₄NO₃S [M+H]⁺: 369.1393, found: 369.1387. FTIR (KBr, cm⁻¹): 3419.88, 3235.00, 1635.50, 1618.69, 1397.39, 1176.10.



(2Z, 5E)-2, 4-dimethyl-N-(methylsulfonyl)-6-phenylhexa-2, 5-dienamide (3oa): Following the general procedure, **3oa** was obtained as a light yellow liquid, yield = 83%. ¹H NMR (500 MHz, CDCl₃): δ = 1.22 (d, *J* = 7.0 Hz, 3H), 1.97 (d, *J* = 1.0 Hz, 3H),

3.33 (s, 3H), 3.78-3.71 (m, 1H), 5.80 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.13 (dd, *J* = 16.0 Hz, *J* = 7.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.37-7.28 (m, 4H), 8.16 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.36, 19.99, 36.21, 40.73, 125.22, 126.39, 126.48, 127.54, 128.71, 131.53, 135.88, 143.08, 165.93. HRMS (ESI): *m/z* for C₁₅H₂₀NO₃S [M+H]⁺: 294.1158, found: 294.1153. FTIR (KBr, cm⁻¹): 3444.68, 3226.17, 2923.36, 1642.06, 1398.13.



3pa

(2Z, 5E)-N-methoxy-2, 4-dimethyl-6-phenylhexa-2, 5-dienamide (3pa): Following the general procedure, **3pa** was obtained

as a light yellow liquid, yield = 87%. ¹H NMR (500 MHz, CDCl₃):

δ = 1.19 (d, J = 7.0 Hz, 3H), 1.93 (d, J = 1.5 Hz, 3H), 3.52-3.41 (m,

1H), 3.81 (s, 3H), 5.52 (dd, J = 10.0 Hz, J = 1.0 Hz, 1H), 6.16 (dd, J = 16.0 Hz, J =

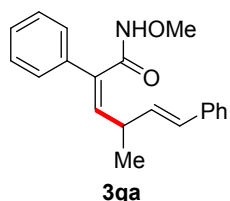
7.0 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 7.23-7.20 (m, 1H), 7.32-7.28 (m, 2H), 7.36-

7.34 (m, 2H), 8.34 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.55, 20.14, 36.30, 63.55,

125.13, 126.33, 127.54, 127.82, 132.89, 136.10, 136.80. HRMS (ESI): m/z for

C₁₅H₂₀NO₂ [M+H]⁺: 246.1489, found: 246.1494. FTIR (KBr, cm⁻¹): 3444.99, 3192.65,

2951.53, 2362.75, 1663.42, 1401.08.



3qa

(2Z, 5E)-N-methoxy-4-methyl-2, 6-diphenylhexa-2, 5-dienamide (3qa): Following the general procedure, **3qa** was obtained

as a light yellow liquid, yield = 79%. ¹H NMR (500 MHz, CDCl₃):

δ = 1.28 (d, J = 6.5 Hz, 3H), 3.61-3.57 (m, 1H), 3.80 (s, 3H), 5.99

(d, J = 10.5 Hz, 1H), 6.20 (dd, J = 16.0 Hz, J = 6.5 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H),

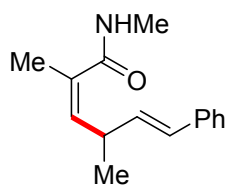
7.19 (t, J = 7.0 Hz, 1H), 7.38-7.26 (m, 9H), 8.58 (s, 1H). ¹³C NMR (125 Hz, CDCl₃):

δ = 20.85, 37.64, 64.47, 126.21, 126.35, 127.34, 128.15, 128.56, 128.72, 129.23,

133.19, 133.62, 136.50, 137.23, 138.27, 166.35. HRMS (ESI): m/z for C₂₀H₂₂NO₂

[M+H]⁺: 308.1645, found: 308.1651. FTIR (KBr, cm⁻¹): 3473.51, 3414.90, 3234.58,

1615.58, 1400.93.



3ra

(2Z, 5E)-N, 2, 4-trimethyl-6-phenylhexa-2, 5-dienamide (3ra): Following the general procedure, **3ra** was obtained as a light

yellow liquid, yield = 17%. ¹H NMR (500 MHz, CDCl₃): δ = 1.18

(d, J = 7.0 Hz, 1H), 1.93 (d, J = 1.5 Hz, 3H), 2.87 (d, J = 5.0 Hz,

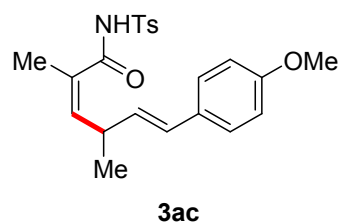
3H), 3.53-3.46 (m, 1H), 5.44 (dd, J = 9.5 Hz, J = 1.5 Hz, 1H),

5.95 (s, 1H), 6.18 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 7.21 (t,

J = 7.0 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.35 (d, J = 7.0 Hz, 1H). ¹³C NMR (125 Hz,

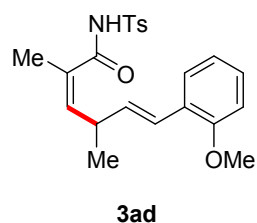
CDCl₃): δ = 20.93, 21.25, 26.09, 37.19, 126.12, 127.26, 128.39, 128.55, 131.77,

134.39, 135.88, 137.26, 170.58. HRMS (ESI): m/z for $C_{15}H_{20}NO$ $[M+H]^+$: 230.1539, found: 230.1545. FTIR (KBr, cm^{-1}): 3550.32, 3415.54, 2924.61, 1635.01, 1402.64.



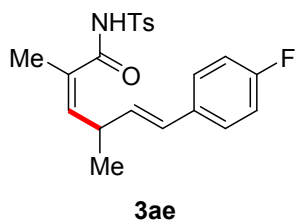
(2Z,5E)-6-(4-methoxyphenyl)-2,4-dimethyl-N-tosylhexa-2,5-dienamide (3ac): Following the general procedure, **3ac** was obtained as a white liquid, yield = 94%. 1H NMR (500 MHz, $CDCl_3$): δ = 1.12 (d, J = 6.5

Hz, 3H), 1.86 (d, J = 1.5 Hz, 3H), 2.42 (s, 3H), 3.50-3.43 (m, 1H), 3.79 (s, 3H), 5.63 (dd, J = 10.0 Hz, J = 1.5 Hz, 1H), 5.91 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H), 6.31 (d, J = 15.5 Hz, 1H), 6.84-6.81 (m, 2H), 7.26 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 19.22, 20.02, 20.65, 36.04, 54.27, 112.96, 126.37, 126.98, 127.46, 127.89, 128.55, 128.77, 129.57, 134.68, 141.43, 144.05, 158.09, 165.13. HRMS (ESI): m/z for $C_{22}H_{26}NO_4S$ $[M+H]^+$: 400.1577, found: 400.1573. FTIR (KBr, cm^{-1}): 3472.88, 3415.50, 2957.14, 2920.69, 1616.97, 1171.18.

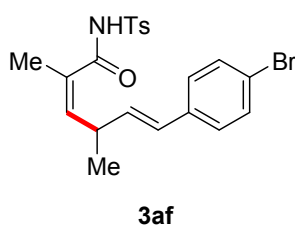


(2Z,5E)-6-(2-methoxyphenyl)-2,4-dimethyl-N-tosylhexa-2,5-dienamide (3ad): Following the general procedure, **3ad** was obtained as a yellow liquid, yield = 89%. 1H NMR (500

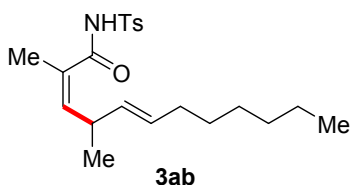
MHz, $CDCl_3$): δ = 1.12 (d, J = 6.5 Hz, 3H), 1.87 (d, J = 1.5 Hz, 3H), 2.42 (s, 3H), 3.46-3.39 (m, 1H), 3.84 (s, 3H), 5.64 (dd, J = 10.0 Hz, J = 1.5 Hz, 1H), 6.08 (dd, J = 16.5 Hz, J = 7.0 Hz, 1H), 6.67 (d, J = 16.0 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 7.22-7.18 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.36 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.98 (d, J = 8.5 Hz, 2H), 8.47 (s, 1H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 19.23, 19.95, 20.64, 36.38, 54.43, 109.82, 119.61, 123.28, 125.04, 125.76, 127.11, 127.44, 128.53, 132.66, 134.72, 141.02, 143.99, 155.55, 165.27. HRMS (ESI): m/z for $C_{22}H_{26}NO_4S$ $[M+H]^+$: 400.1577, found: 400.1579. FTIR (KBr, cm^{-1}): 3550.21, 3473.77, 3415.14, 2920.56, 1615.76, 1168.22.



(2Z, 5E)-6-(4-fluorophenyl)-2, 4-dimethyl-N-tosylhexa-2, 5-dienamide (3ae): Following the general procedure, **3ae** was obtained as a white liquid, yield = 90%. ¹H NMR (500 MHz, CDCl₃): δ = 1.14 (d, *J* = 7.0 Hz, 3H), 1.87 (d, *J* = 1.5 Hz, 3H), 2.44 (s, 3H), 3.57-3.49 (m, 1H), 5.65 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 5.98 (dd, *J* = 15.5 Hz, *J* = 7.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.98 (m, 2H), 7.32 (m, 4H), 7.98 (d, *J* = 8.0 Hz, 2H), 8.29 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.29, 19.90, 20.68, 36.03, 114.30, 114.47, 126.70 (d, *J*_{C-F} = 7.9 Hz), 127.02, 127.33, 128.57, 131.42 (d, *J*_{C-F} = 2.0 Hz), 132.10 (d, *J*_{C-F} = 3.3 Hz), 134.52, 141.47, 144.15, 161.18 (d, *J*_{C-F} = 245.0 Hz), 164.84. HRMS (ESI): *m/z* for C₂₁H₂₃FNO₃S [M+H]⁺: 388.1377, found: 388.1377. FTIR (KBr, cm⁻¹): 3450.59, 2931.91, 1853.40, 1650.61, 1401.08.

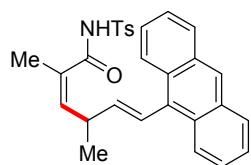


(2Z, 5E)-6-(4-bromophenyl)-2, 4-dimethyl-N-tosylhexa-2, 5-dienamide (3af): Following the general procedure, **3af** was obtained as a white solid, m.p.: 86.0 °C, yield = 90%. ¹H NMR (500 MHz, CDCl₃): δ = 1.13 (d, *J* = 7.0 Hz, 3H), 1.87 (d, *J* = 1.0 Hz, 3H), 2.43 (s, 3H), 3.58-3.52 (m, 1H), 5.64 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.05 (dd, *J* = 16.0 Hz, *J* = 8.5 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.37 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.27, 19.71, 20.69, 35.96, 120.06, 126.74, 127.04, 127.26, 127.45, 128.58, 130.55, 132.53, 134.50, 134.95, 141.41, 144.16, 164.87. HRMS (ESI): *m/z* for C₂₁H₂₃BrNO₃S [M+H]⁺: 448.0577, found: 448.0568. FTIR (KBr, cm⁻¹): 3550.29, 3415.35, 1635.66, 1616.12, 1409.19, 612.72.



(2Z, 5E)-2, 4-dimethyl-N-tosyl-dodeca-2, 5-dienamide (3ab): Following the general procedure, **3ab** was obtained as a white liquid, yield = 69%. ¹H NMR (500 MHz, CDCl₃): δ = 0.89 (t, *J* = 6.5 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 1.31-1.26 (m, 6H), 1.38-1.34 (m, 2H), 1.84 (d, *J* = 1.0 Hz, 3H), 2.02-1.98 (m, 2H), 2.44 (s, 3H), 3.27-3.17 (m, 1H), 5.35 (dd, *J* = 15.5 Hz, *J* = 7.0 Hz, 1H),

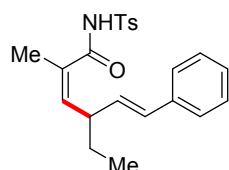
5.51-5.45 (m, 1H), 5.58 (dd, $J = 10.0$ Hz, $J = 1.5$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.97 (d, $J = 8.5$ Hz, 2H), 8.32 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 13.08, 19.23, 20.45, 20.67, 21.59, 27.86, 28.25, 30.67, 31.49, 35.94, 127.28, 127.48, 128.53, 130.10, 131.93, 134.68, 141.24, 144.02, 165.07$. HRMS (ESI): m/z for $\text{C}_{21}\text{H}_{32}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 378.2097, found: 378.2107. FTIR (KBr, cm^{-1}): 3439.25, 2959.81, 2931.78, 2858.88, 1692.52, 1416.70, 1170.21, 1086.92, 671.96.



3ah

(2Z, 5E)-6-(anthracen-9-yl)-2,4-dimethyl-N-tosylhexa-2,5-dienamide (3ah): Following the general procedure, **3ah** was obtained as a yellow liquid, yield = 78%. ^1H NMR (500 MHz, CDCl_3): $\delta = 1.31$ (d, $J = 6.5$ Hz, 3H), 1.97 (d, $J = 1.0$ Hz, 3H),

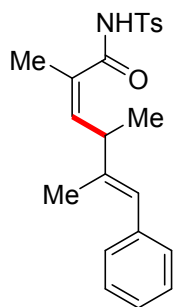
2.27 (s, 3H), 3.93-3.85 (m, 2H), 5.88-5.83 (m, 2H), 6.96 (d, $J = 16.5$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.47-7.44 (m, 4H), 7.99-7.97 (m, 4H), 8.18-8.14 (m, 2H), 8.35 (s, 1H), 8.40 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 19.41, 20.07, 20.52, 36.48, 123.97, 124.05, 124.34, 124.81, 125.14, 126.94, 127.45, 127.57, 128.40, 128.52, 130.36, 131.52, 134.45, 140.27, 142.34, 144.13, 164.75$. HRMS (ESI): m/z for $\text{C}_{29}\text{H}_{28}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 470.1784, found: 470.1780. FTIR (KBr, cm^{-1}): 3415.56, 2923.36, 1615.87, 1400.93, 615.89.



3ai

(2Z, 5E)-4-ethyl-2-methyl-6-phenyl-N-tosylhexa-2,5-dienamide (3ai): Following the general procedure, **3ai** was obtained as a yellow liquid, yield = 37%. ^1H NMR (500 MHz, CDCl_3): $\delta = 0.83$ (t, $J = 7.5$ Hz, 3H), 1.50-1.43 (m, 2H), 1.87 (d, $J = 1.5$ Hz,

3H), 2.44 (s, 3H), 3.24-3.17 (m, 1H), 5.65 (dd, $J = 10.0$ Hz, $J = 1.5$ Hz, 1H), 5.99 (dd, $J = 16.0$ Hz, $J = 8.0$ Hz, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 7.23 (t, $J = 7.0$ Hz, 1H), 7.37-7.29 (m, 6H), 7.98 (d, $J = 8.5$ Hz, 2H), 8.19 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 10.52, 19.31, 20.66, 27.60, 43.67, 125.25, 126.49, 127.50, 127.54, 128.41, 128.54, 129.74, 130.17, 134.67, 135.90, 139.42, 144.09, 165.03$. HRMS (ESI): m/z for $\text{C}_{22}\text{H}_{26}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 384.1628, found: 384.1620. FTIR (KBr, cm^{-1}): 3550.12, 3238.30, 2965.42, 2926.17, 1634.84, 1615.85, 1403.49, 1167.79, 1081.31.



3aj

(2Z, 5E)-2, 4, 5-trimethyl-6-phenyl-N-tosylhexa-2, 5-dienamide

(3aj): Following the general procedure, **3aj** was obtained as a white

liquid, yield = 49%. ¹H NMR (500 MHz, CDCl₃): δ = 1.19 (d, *J* = 6.5

Hz, 3H), 1.82 (d, *J* = 1.5 Hz, 3H), 1.89 (d, *J* = 1.0 Hz, 3H), 2.43 (s,

3H), 3.36-3.30 (m, 1H), 5.78 (dd, *J* = 10.0 Hz, *J* = 1.5 Hz, 1H), 6.34 (s,

1H), 7.26-7.20 (m, 3H), 7.35-7.32 (m, 4H), 7.98 (d, *J* = 8.0 Hz, 2H),

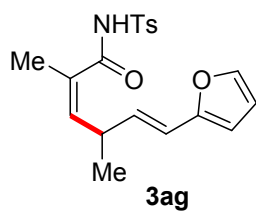
8.36 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 14.65, 19.03, 19.35, 20.66, 41.66,

124.73, 125.45, 127.11, 127.52, 127.93, 128.45, 128.55, 134.67, 136.53, 140.44,

140.84, 144.09, 165.06. HRMS (ESI): *m/z* for C₂₂H₂₆NO₃S [M+H]⁺: 384.1628, found:

384.1638. FTIR (KBr, cm⁻¹): 3442.06, 2965.42, 2926.17, 1653.27, 1403.74, 1162.62,

739.25.



3ag

(2Z, 5E)-6-(furan-2-yl)-2, 4-dimethyl-N-tosylhexa-2, 5-dien

amide (3ag): Following the general procedure, **3ag** was

obtained as a brown liquid, yield = 67%. ¹H NMR (500 MHz,

CDCl₃): δ = 1.11 (d, *J* = 7.0 Hz, 3H), 1.87 (d, *J* = 1.5 Hz, 3H),

2.44 (s, 3H), 3.53-3.46 (m, 1H), 5.62 (dd, *J* = 10.0 Hz, *J* = 1.0 Hz, 1H), 6.00 (dd, *J* =

16.0 Hz, *J* = 7.5 Hz, 1H), 6.19-6.15 (m, 2H), 6.35 (dd, *J* = 3.5 Hz, *J* = 2.0 Hz, 1H),

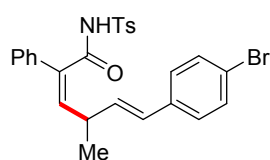
7.31 (d, *J* = 1.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 8.18 (s,

1H). ¹³C NMR (125 Hz, CDCl₃): δ = 19.28, 19.77, 20.68, 35.72, 106.54, 110.25,

117.03, 126.85, 127.48, 128.57, 130.32, 134.53, 140.67, 141.50, 144.13, 151.42,

164.80. HRMS (ESI): *m/z* for C₁₉H₂₂NO₄S [M+H]⁺: 360.1264, found: 360.1247.

FTIR (KBr, cm⁻¹): 3415.64, 3231.78, 2962.62, 1615.26, 1400.93, 1168.22.



3ef

(R,2Z,5E)-6-(4-bromophenyl)-4-methyl-2-phenyl-N-

tosylhexa-2,5-dienamide (3ef): Following the general

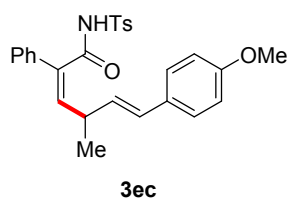
procedure, **3ef** was obtained as a yellow liquid, yield = 93%.

¹H NMR (500 MHz, CDCl₃): δ = 1.22 (d, *J* = 7.0 Hz, 3H), 2.47

(s, 3H), 3.67-3.59 (m, 1H), 5.98 (d, *J* = 10.5 Hz, 1H), 6.10 (dd, *J* = 16.0 Hz, *J* = 7.0

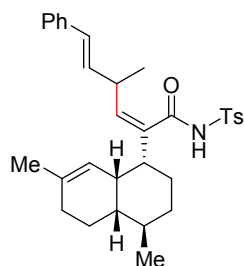
Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 7.15-7.12 (m, 2H), 7.19-7.17 (m, 2H), 7.32-7.28

(m, 3H), 7.37-7.35 (m, 2H), 7.41-7.39 (m, 2H), 7.94 (d, $J = 8.0$ Hz, 2H), 8.10 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 19.41, 20.72, 36.06, 120.00, 126.18, 126.72, 127.46, 127.73, 128.02, 128.58, 130.54, 132.14, 132.97, 134.42, 134.70, 135.08, 141.78, 144.22, 164.01$. HRMS (ESI): m/z for $\text{C}_{26}\text{H}_{25}\text{BrNO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 510.0733, found: 510.0721. FTIR (KBr, cm^{-1}): 3453.40, 3414.15, 2923.50, 2351.54, 1659.02, 1630.99, 1401.08, 1179.59.



(R,2Z,5E)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-N-tosylhexa-2,5-dienamide (3ec): Following the general procedure, **3ef** was obtained as a yellow liquid, yield = 91%.

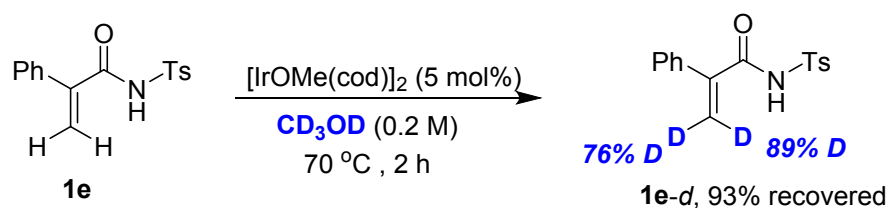
^1H NMR (500 MHz, CDCl_3): $\delta = 1.20$ (d, $J = 6.5$ Hz, 1H), 2.45 (s, 3H), 3.58-3.51 (m, 1H), 3.77 (s, 3H), 6.00-5.93 (m, 2H), 6.29 (d, $J = 16.0$ Hz, 1H), 6.83-6.80 (m, 2H), 7.15-7.13 (m, 2H), 7.30-7.23 (m, 5H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.94 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 19.61, 20.70, 36.14, 54.25, 112.91, 126.05, 126.60, 127.45, 127.56, 127.93, 128.55, 128.90, 129.14, 132.65, 134.48, 134.74, 141.71, 144.14, 157.97, 164.26$. HRMS (ESI): m/z for $\text{C}_{27}\text{H}_{28}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$: 462.1734, found: 462.1729. FTIR (KBr, cm^{-1}): 3470.22, 3237.51, 2962.75, 2926.30, 1614.16, 1510.43, 1423.51, 1176.78, 809.50, 666.51.



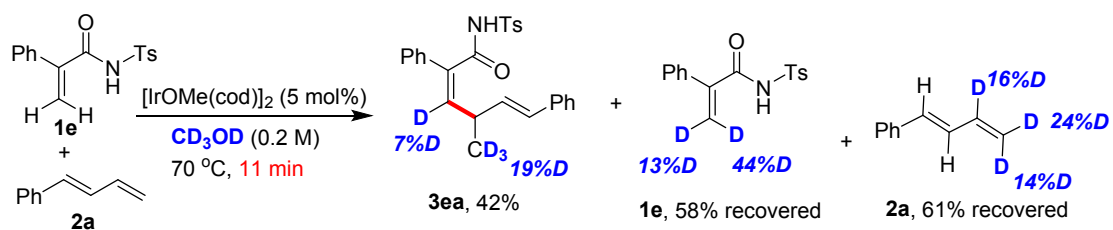
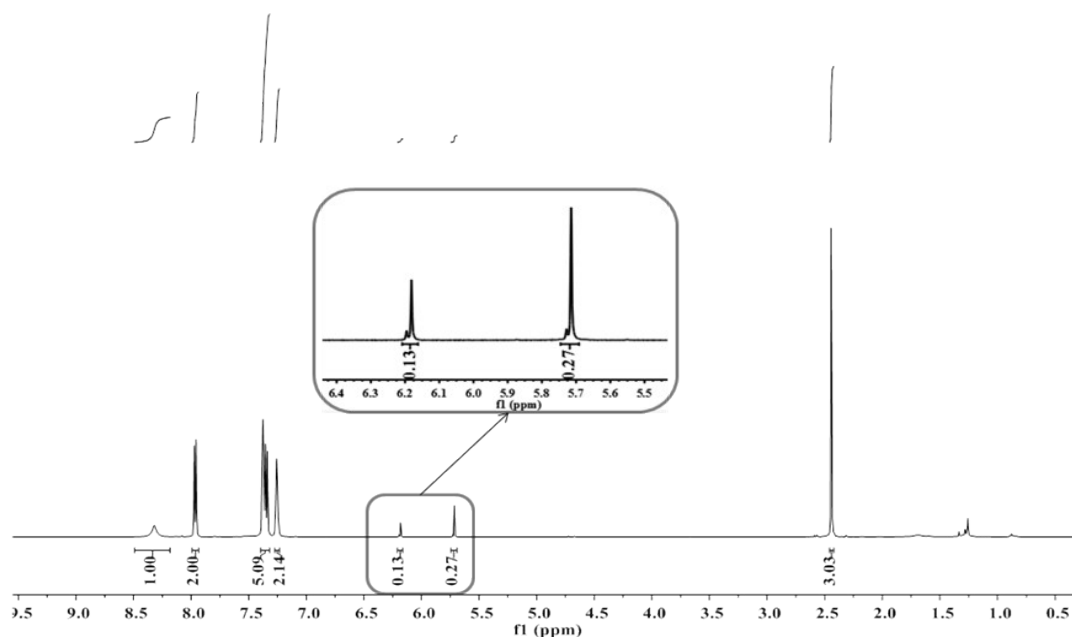
Following the general procedure, **3sa** was obtained as a white solid, m.p.: 68.5 °C, yield = 61%. ^1H NMR (500 MHz, CDCl_3): $\delta = 0.84$ (d, $J = 6.5$ Hz, 3H), 1.00-0.94 (m, 1H), 1.13 (d, $J = 7.0$ Hz, 3H), 1.22-1.16 (m, 2H), 1.36-1.27 (m, 2H), 1.42-1.38 (m, 1H), 1.58 (s, 3H), 1.75-1.64 (m, 2H), 1.86-1.81 (m, 2H), 1.94 (s, 1H), 2.43 (s, 3H), 2.48-2.45 (m, 1H), 3.28-3.21 (s, 1H), 4.91 (s, 1H), 5.35 (dd, $J = 10.0$ Hz, $J = 1.5$ Hz, 1H), 6.20 (dd, $J = 16.0$ Hz, $J = 6.5$ Hz, 1H), 6.51 (d, $J = 16.0$ Hz, 1H), 7.26-7.24 (m, 1H), 7.35-7.29 (m, 4H), 7.41 (d, $J = 7.5$ Hz, 2H), 7.92 (d, $J = 8.5$ Hz, 2H), 8.08 (s, 1H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 18.57, 20.50, 20.67, 22.92, 24.06,$

24.12, 25.34, 26.40, 33.83, 36.67, 36.87, 40.07, 42.95, 118.22, 125.30, 126.61, 127.46, 127.63, 128.43, 128.58, 132.29, 134.10, 134.54, 134.98, 135.77, 137.17, 144.06, 166.49. HRMS (ESI): m/z for $C_{32}H_{40}NO_3S$ $[M+H]^+$: 518.2723, found: 518.2728. FTIR (KBr, cm^{-1}): 3451.20, 2359.95, 1634.28, 1398.28, 501.99.

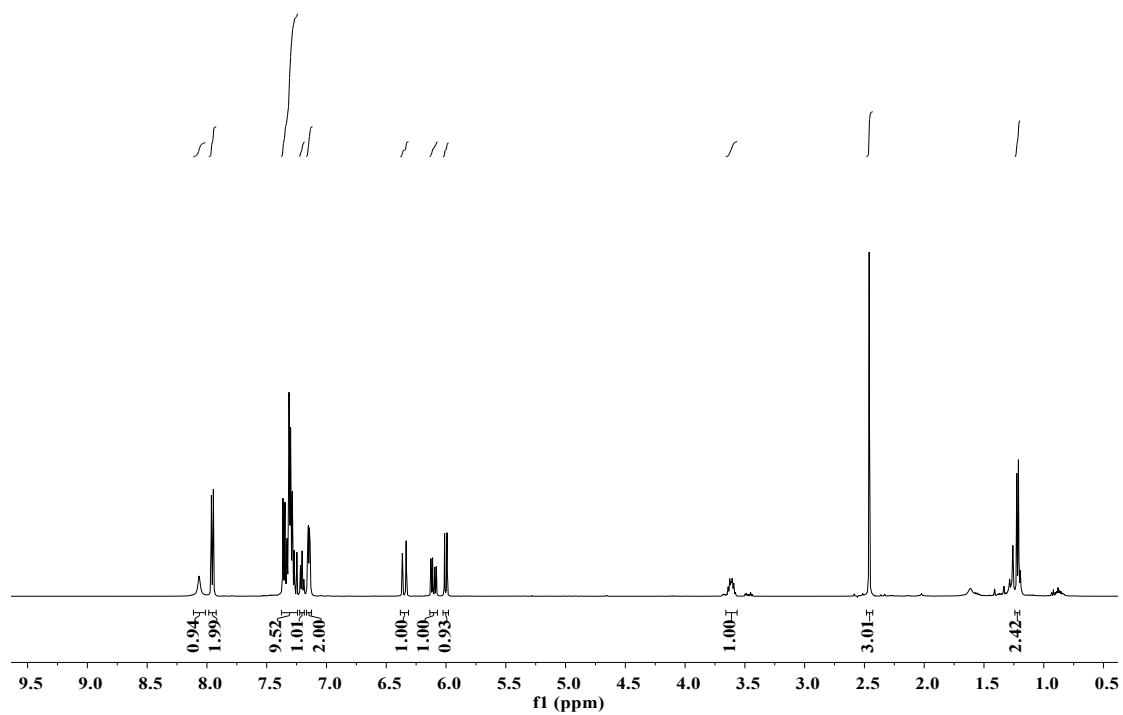
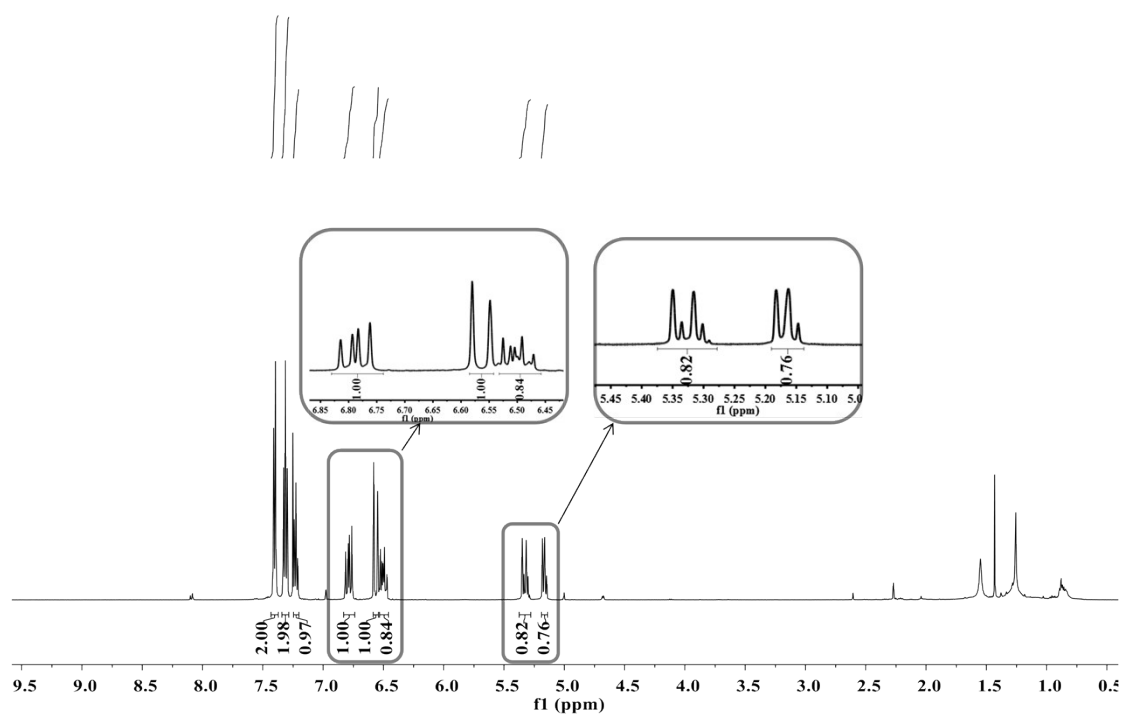
Ir-Catalyzed Deuterium Labelled Experiments

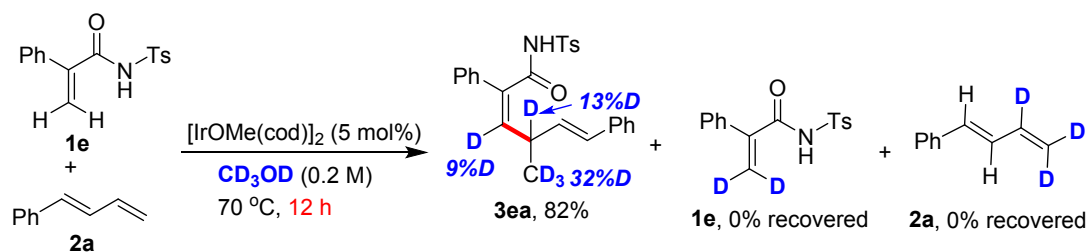
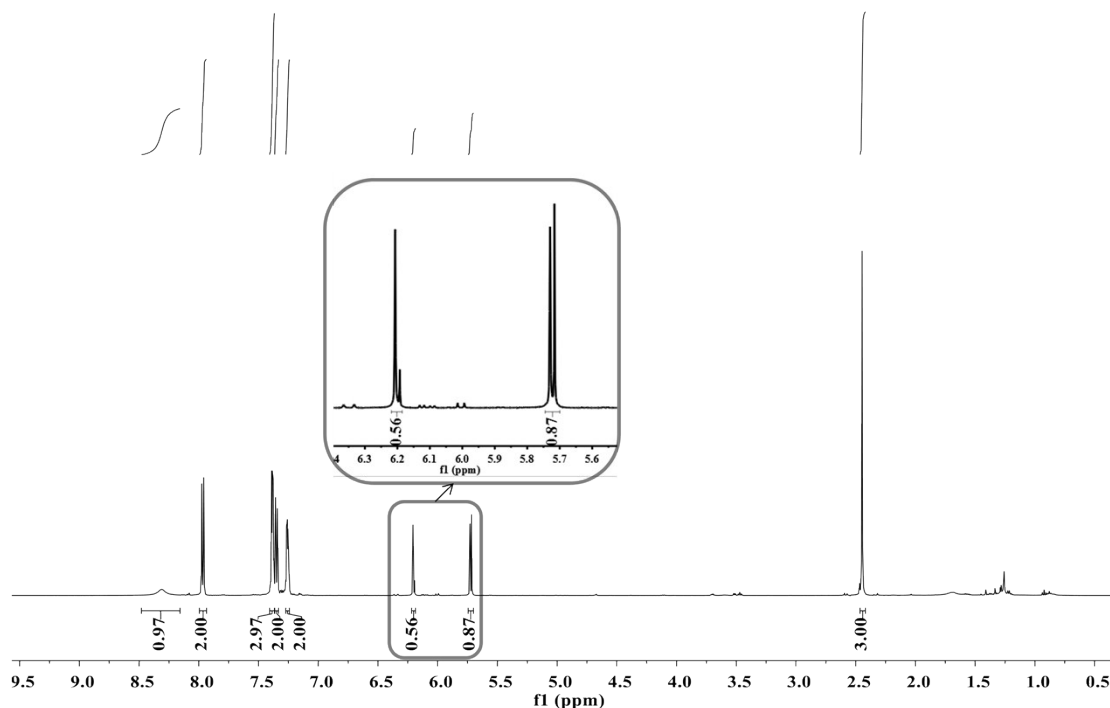


A screw-cap vial was charged with $[\text{IrOMe}(\text{cod})]_2$ (5 mol%) and CD_3OD (1.0 mL). Then, **1e** (1.0 equiv, 0.2 mmol) was added into the solution in sequence. The vial was sealed under argon and heated to 70 °C with stirring for 2 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures) for separation. The D% of **1e-d** was estimated by ^1H NMR.

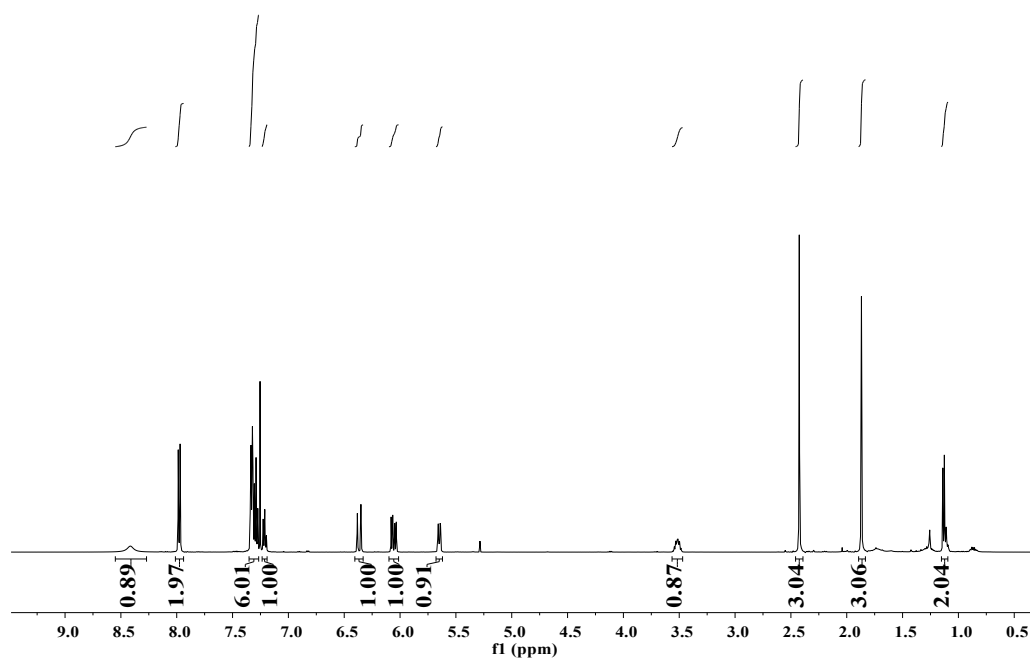


A screw-cap vial was charged with $[\text{IrOMe}(\text{cod})]_2$ (5 mol%) and CD_3OD (1.0 mL). Then, **1e** (1.0 equiv, 0.2 mmol), **2a** (1.2 equiv, 0.24 mmol) was added into the solution in sequence. The vial was sealed under argon and heated to 70 °C with stirring for 11 min. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The D% of product **3ea**, the starting materials **1e** and **2a** were estimated by ^1H NMR.

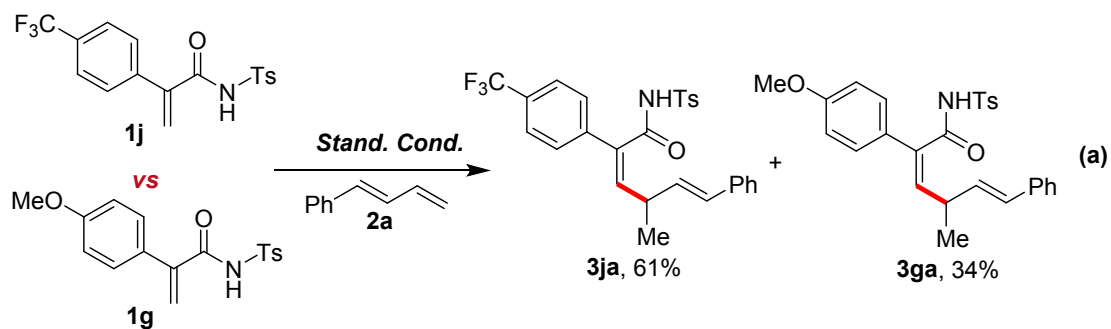




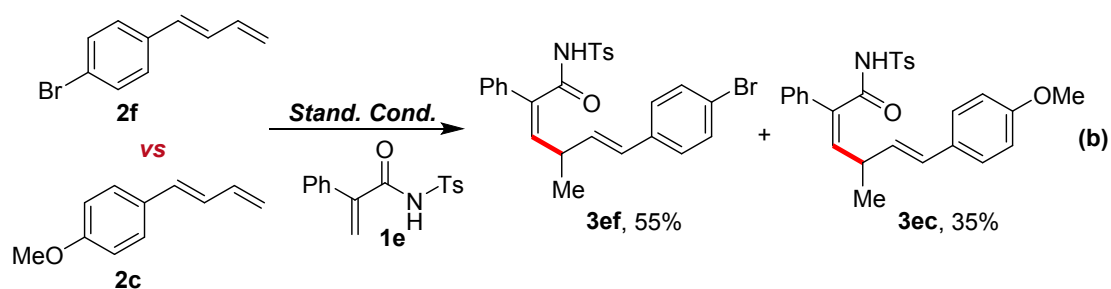
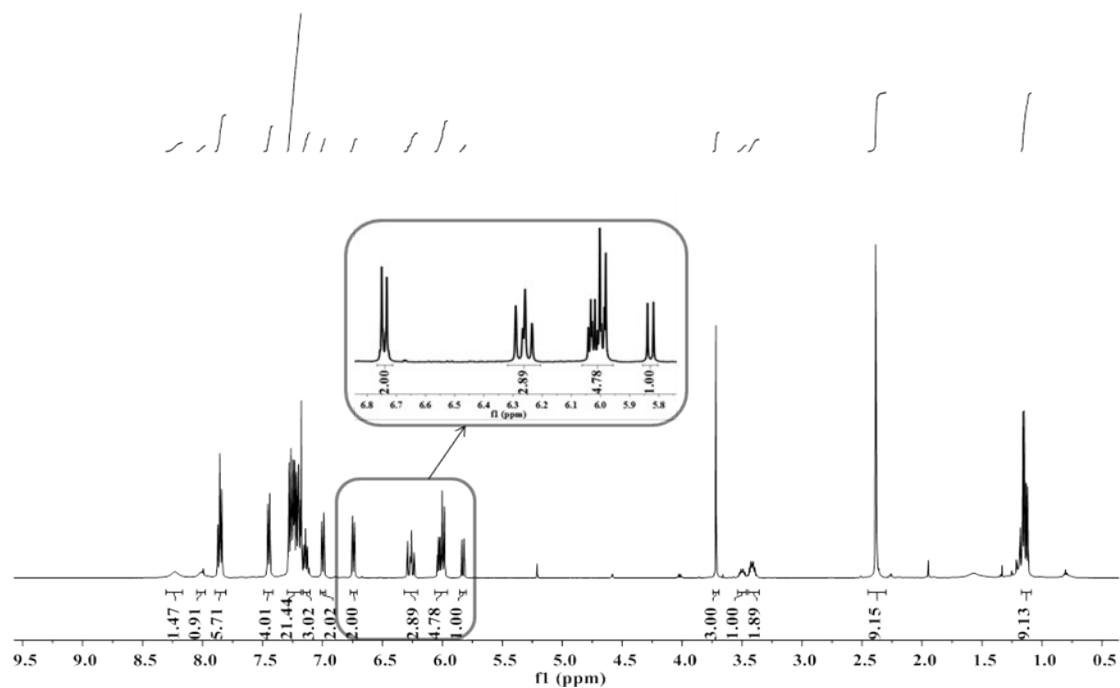
A screw-cap vial was charged with $[\text{IrOMe}(\text{cod})]_2$ (5 mol%) and CD_3OD (1.0 mL). Then, **1e** (1.0 equiv, 0.2 mmol), **2a** (1.2 equiv, 0.24 mmol) was added into the solution in sequence. The vial was sealed under argon and heated to 70 °C with stirring for 12 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The D% of product **3ea** was estimated by ^1H NMR.



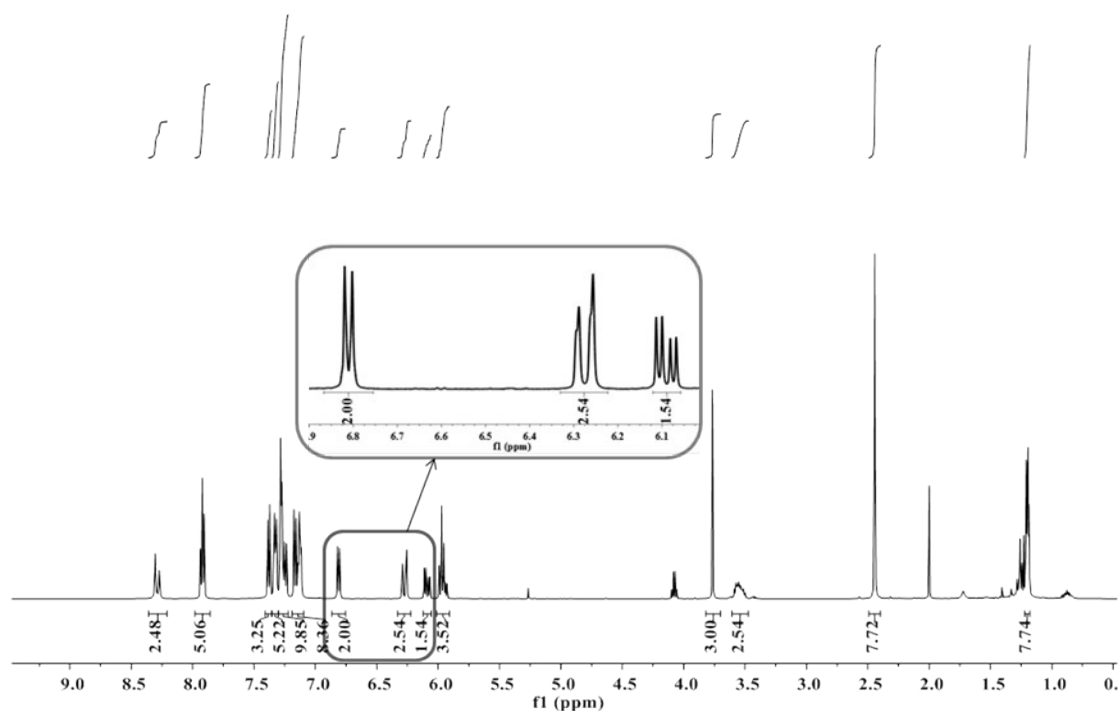
Competition Experiments



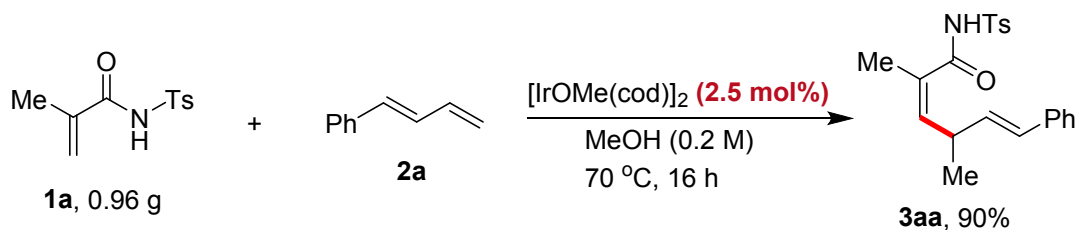
A screw-cap vial was charged with $[\text{IrOMe}(\text{cod})]_2$ (5 mol %, 0.01 mmol) and methanol (1 mL). Then, **2a** (1.0 equiv, 0.2 mmol), **1j** (1.0 equiv, 0.2 mmol) and **1g** (1.0 equiv, 0.2 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 70 °C with stirring for 8 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The product yields were estimated by ^1H NMR.



An screw-cap vial was charged with $[\text{IrOMe}(\text{cod})]_2$ (5 mol %, 0.01 mmol) and methanol (1 mL). Then, **2f** (1.0 equiv, 0.2 mmol), **2c** (1.0 equiv, 0.2 mmol) and **1e** (1.0 equiv, 0.2 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 70 °C with stirring for 8 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The product yields were estimated by ^1H NMR.

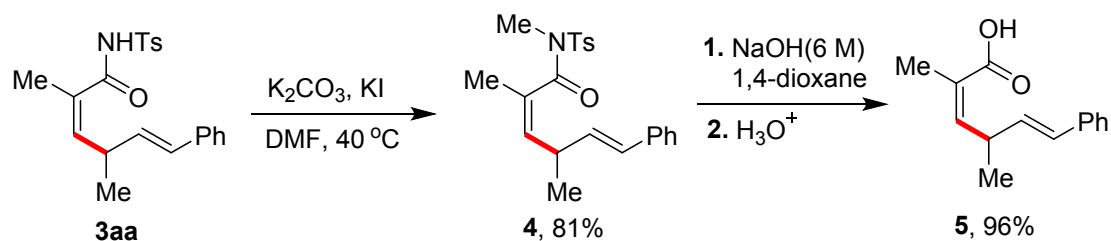


Gram Scaled Synthesis



A screw-cap vial was charged with $[\text{IrOMe(cod)}]_2$ (2.5 mol%) and MeOH (20 mL). Then, **1a** (1.0 equiv, 4.0 mmol, 0.96 g) and **2a** (1.2 equiv, 4.8 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 70 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (ethyl acetate/petroleum ether mixtures). The desired product was obtained as yellow liquid (1.33 g, 90% yield).

Amide Removal



Step 1 K_2CO_3 (27.7 mg, 0.2 mmol), and iodomethane (28.4 mg, 0.2 mmol) were added to a stirred solution of amide **3aa** (37 mg, 0.1 mmol) in DMF (1.0 ml). After stirring at $40\text{ }^\circ\text{C}$ for 3 hours, the solution was cooled to room temperature. Next, water (10 mL) was added and the resulting mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over Na_2SO_4 , filtrated and evaporated. The crude product was purified by silica gel chromatography using petroleum ether/ethyl acetate = 30:1 to give the *N*-Me-*N*-Ts acrylamide **4** as a white liquid (31 mg, 81% yield). 1H NMR (500 MHz, $CDCl_3$): δ = 1.09 (d, J = 6.5 Hz, 3H), 1.86 (d, J = 1.5 Hz, 3H), 2.89-2.82 (m, 1H), 3.28 (s, 3H), 5.36 (dd, J = 10.0 Hz, J = 1.5 Hz, 1H), 5.99 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H), 6.18 (dd, J = 16.0 Hz, J = 1.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.33-7.27 (m, 6H), 7.90 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 Hz, $CDCl_3$): δ = 18.83, 19.57, 20.63, 32.69, 36.51, 125.09, 126.22, 127.42, 127.48, 127.89, 128.48, 129.57, 131.69, 133.70, 134.66, 136.21, 143.88, 170.23.

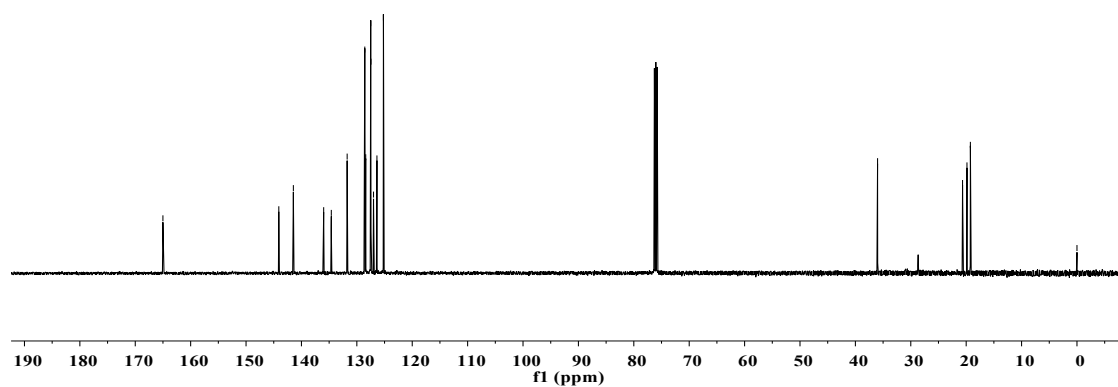
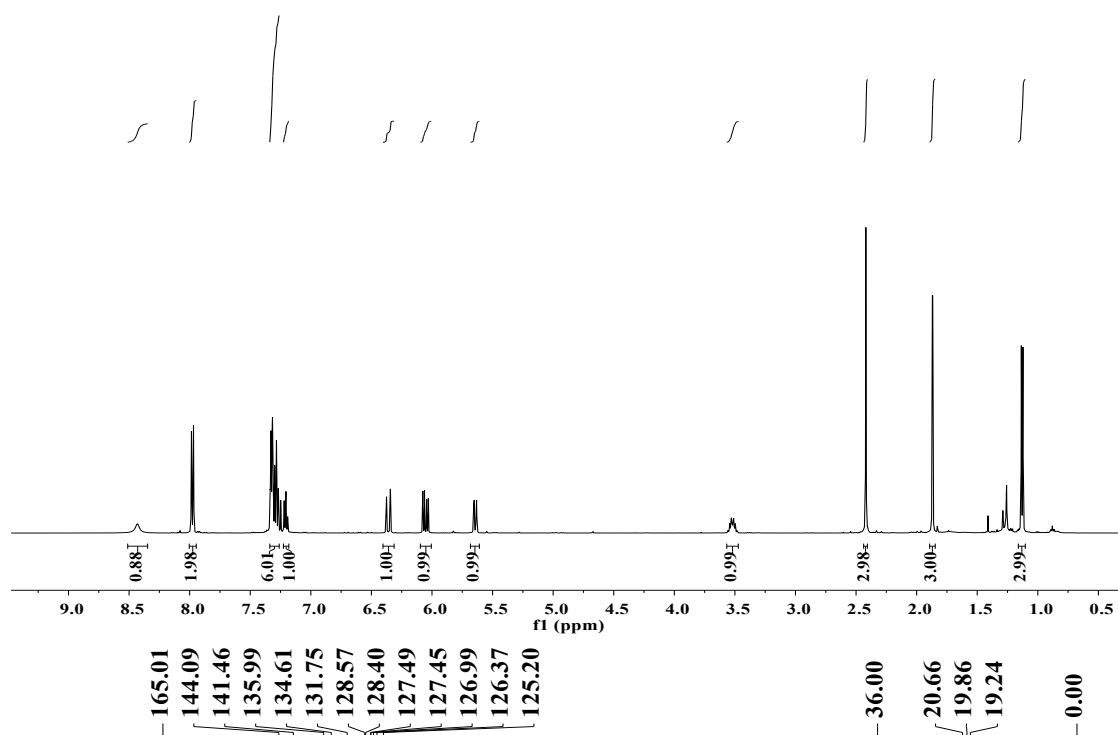
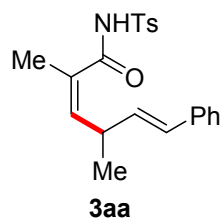
Step 2 *N*-Me-*N*-Ts acrylamide **4** (31 mg, 0.081 mmol) was dissolved in 1,4-dioxane (2.5 mL) and an aqueous solution NaOH (6 M, 2.5 mL) was added. The mixture was heated and stirred at $60\text{ }^\circ\text{C}$ for 16 hours, cooled to room temperature, concentrated and acidified with a aqueous solution of HCl (3 M) and extracted with ethyl acetate (2 x 10 mL). The combined organic layers were dried over Na_2SO_4 , filtrated and evaporated. The crude product was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1 as the eluent to give the product **5**, a light yellow liquid (17 mg, 96% yield). 1H NMR (500 MHz, $CDCl_3$): δ = 1.21 (d, J = 6.5 Hz, 3H), 1.96 (d, J = 1.0 Hz, 3H), 4.23-4.16 (m, 1H), 5.96 (dd, J = 9.0 Hz, J = 1.0 Hz,

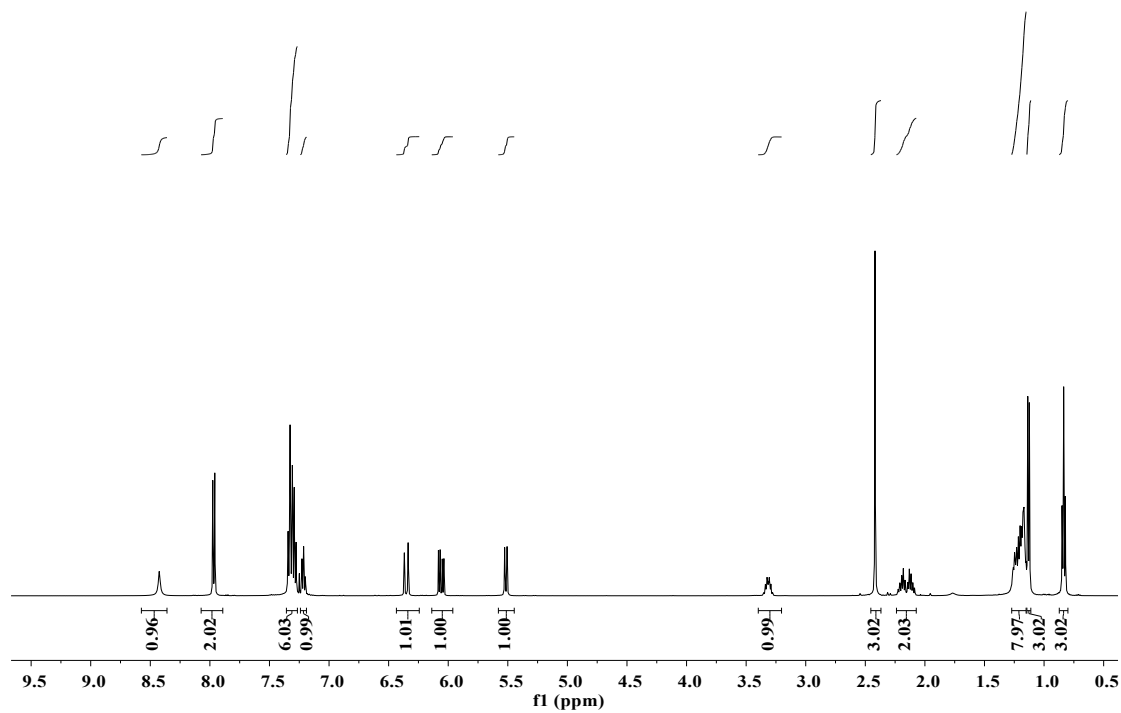
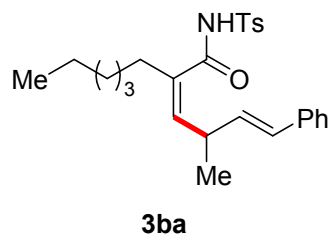
1H), 6.16 (dd, $J = 16.0$ Hz, $J = 6.5$ Hz, 1H), 6.41 (d, $J = 16.0$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 7.0$ Hz, 2H), 7.35 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 20.33, 20.65, 36.51, 124.95, 126.12, 127.11, 128.48, 128.94, 133.36, 137.54, 148.55$.

References

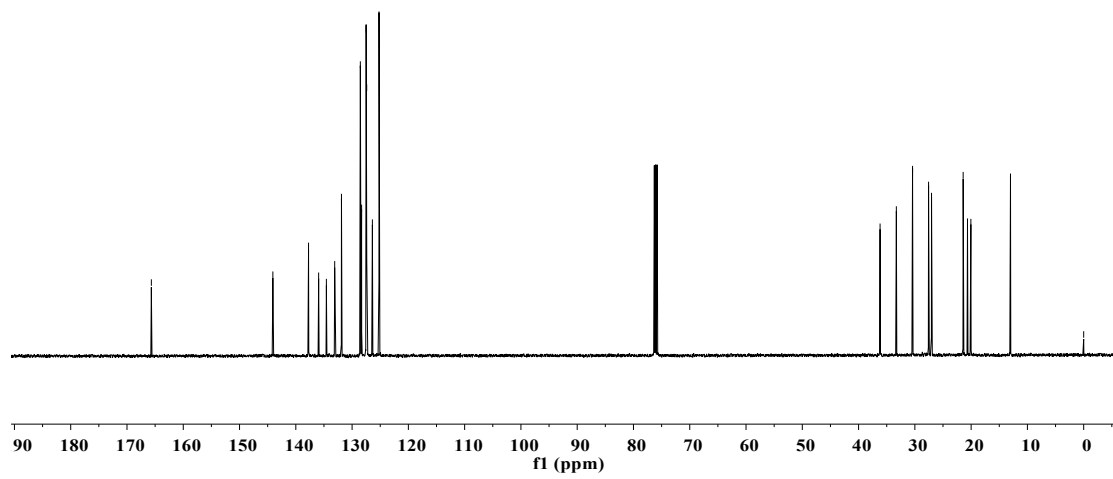
1. S. W. Youn, T. Y. Ko, Y. H. Kim, and Y. A. Kim, *Org. Lett.*, **2018**, *20*, 24.

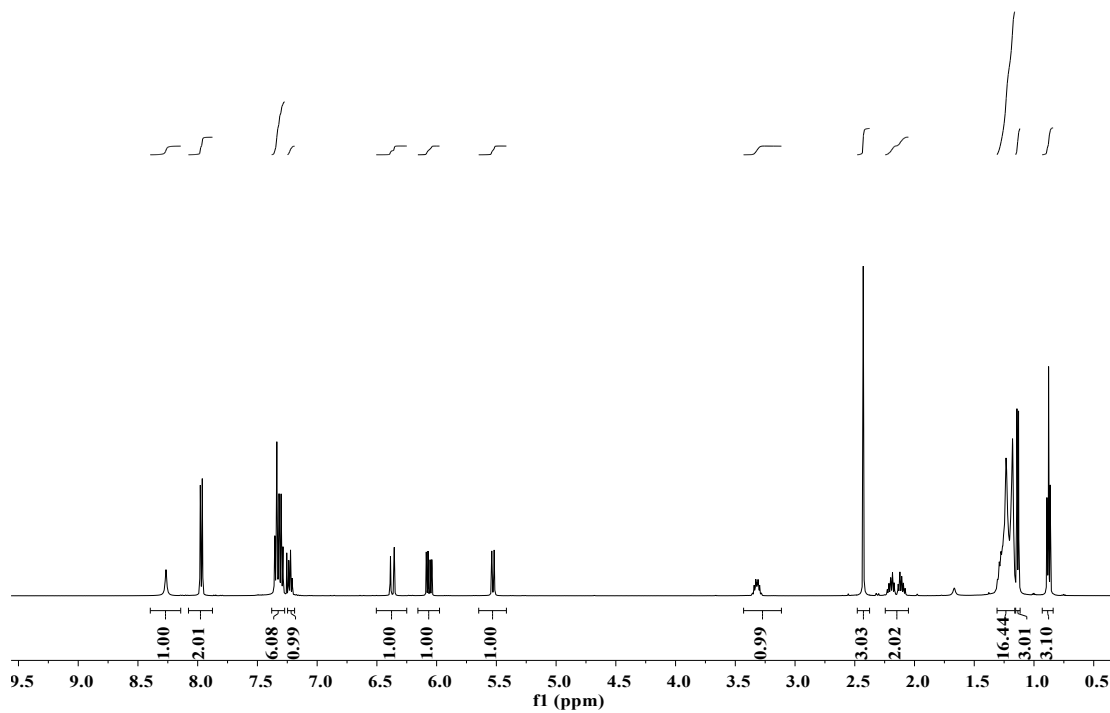
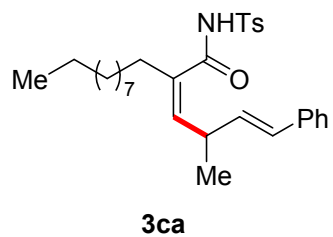
¹H/¹³C NMR Charts





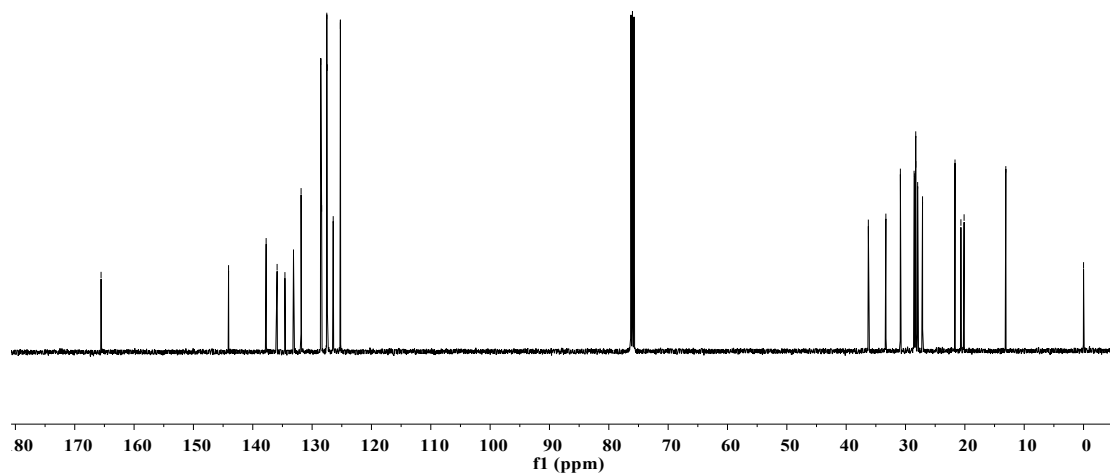
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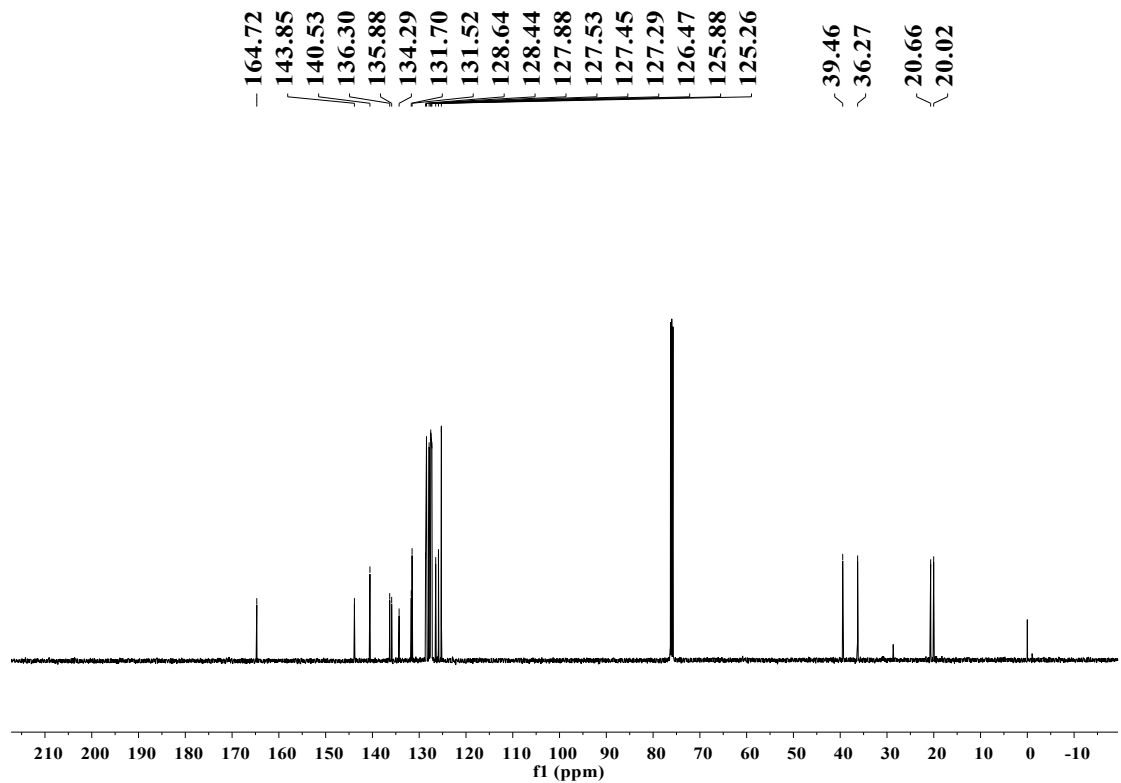
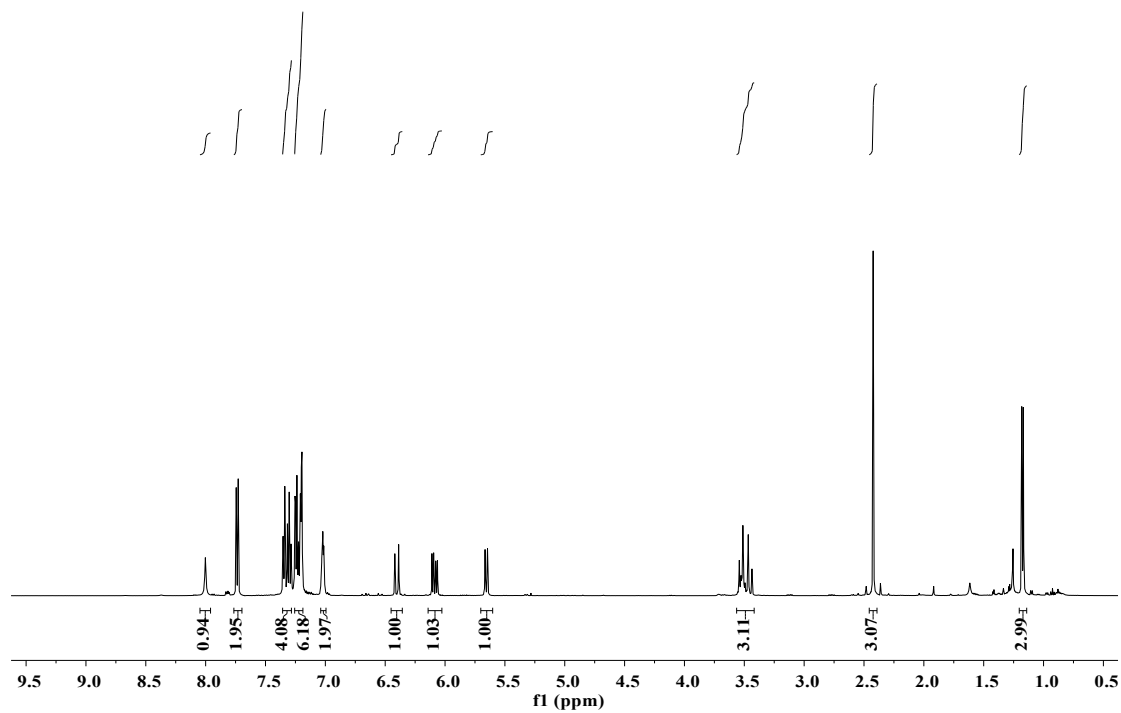
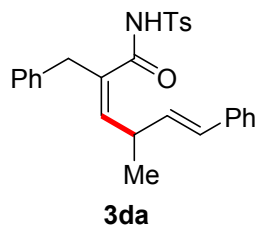


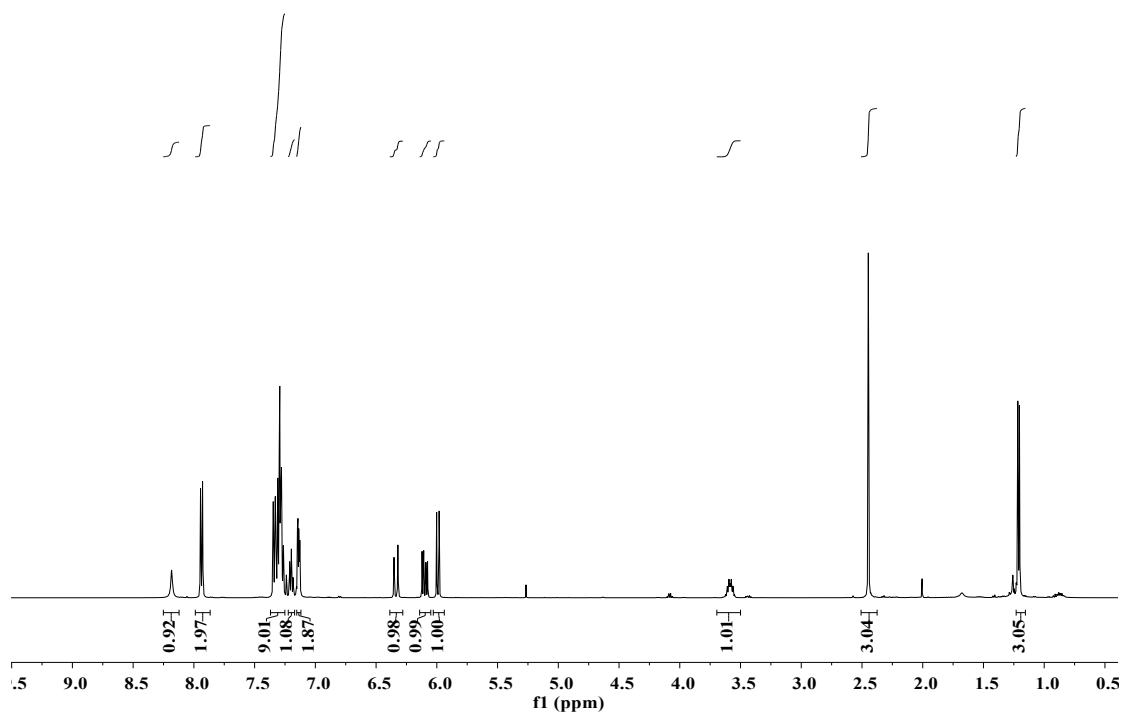
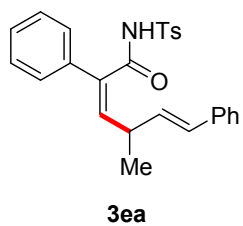


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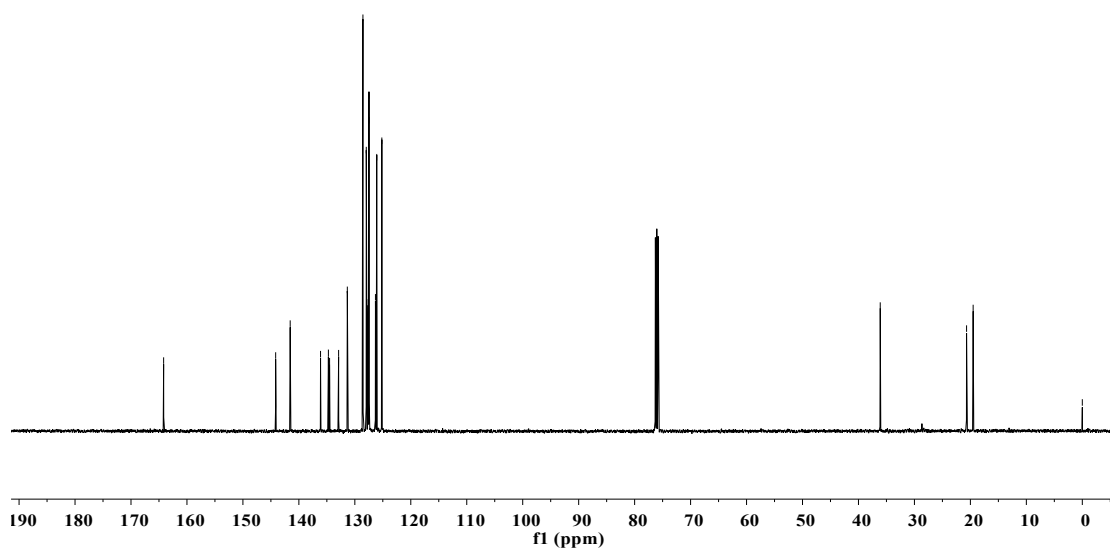


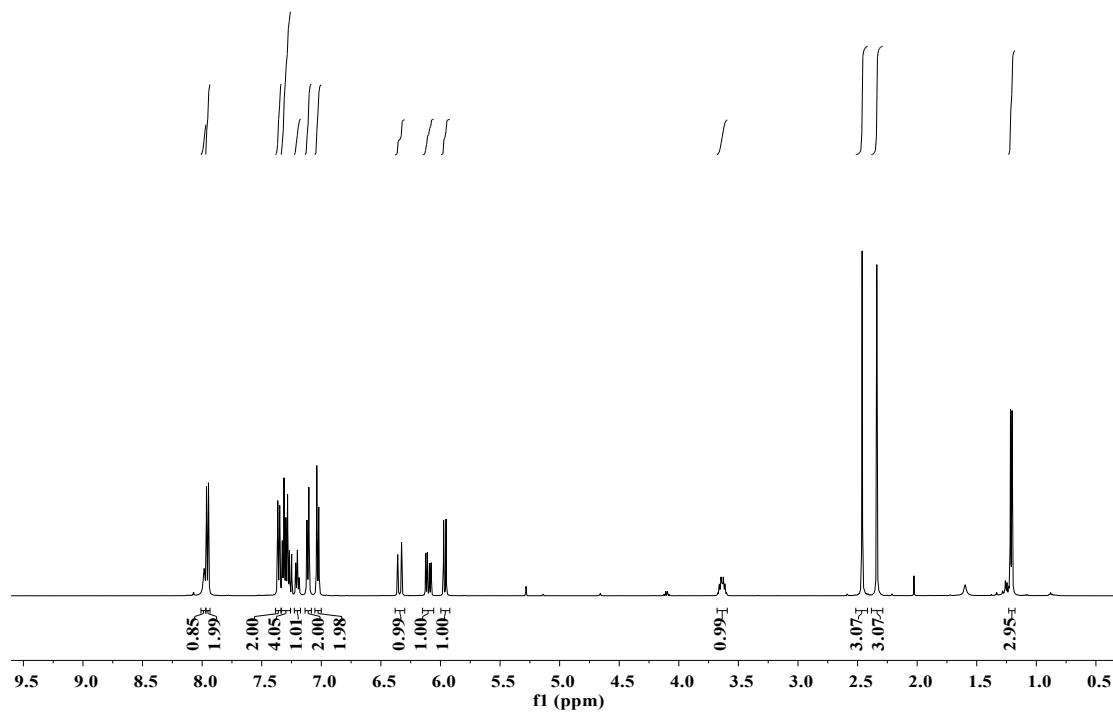
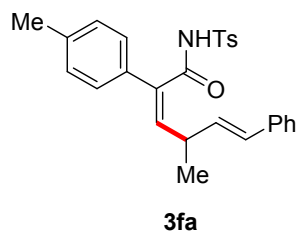
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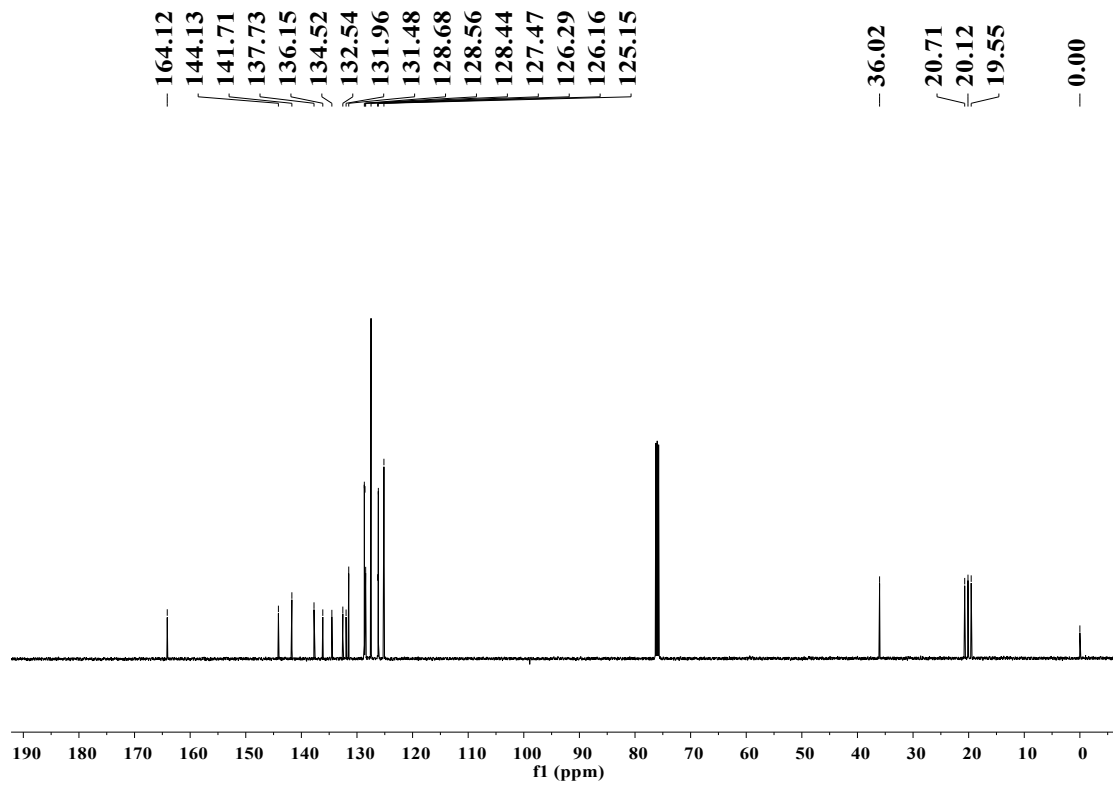
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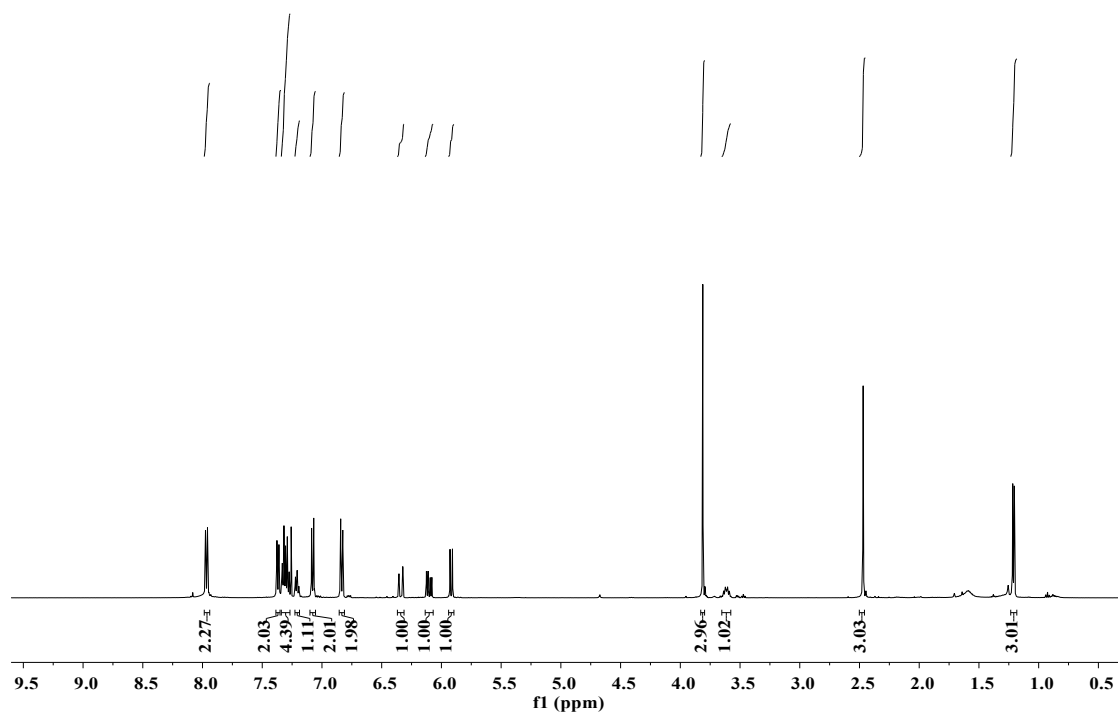
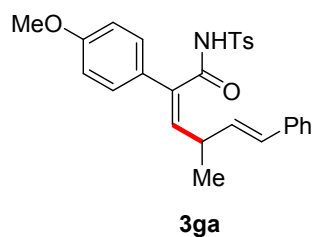
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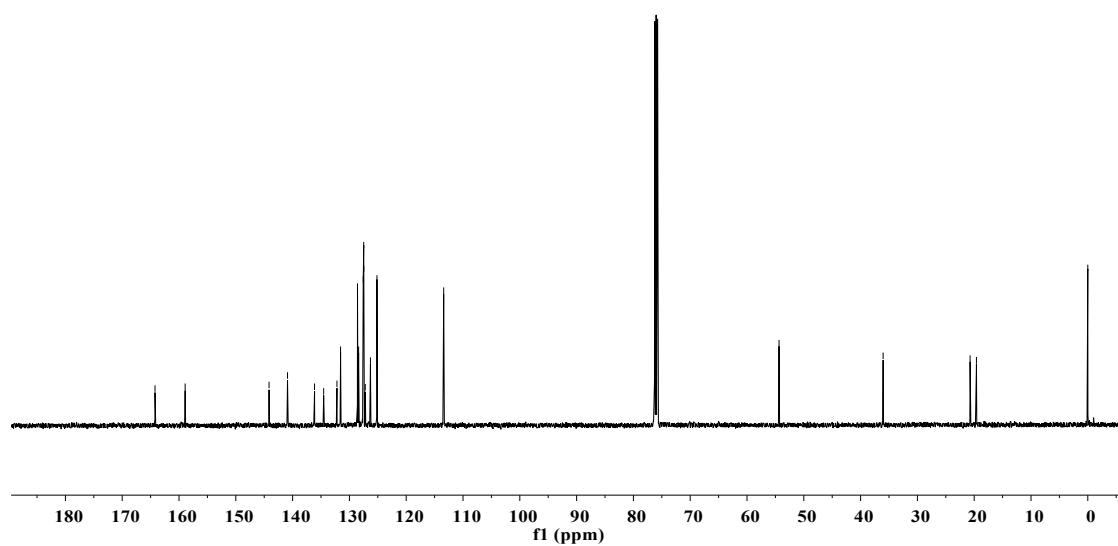


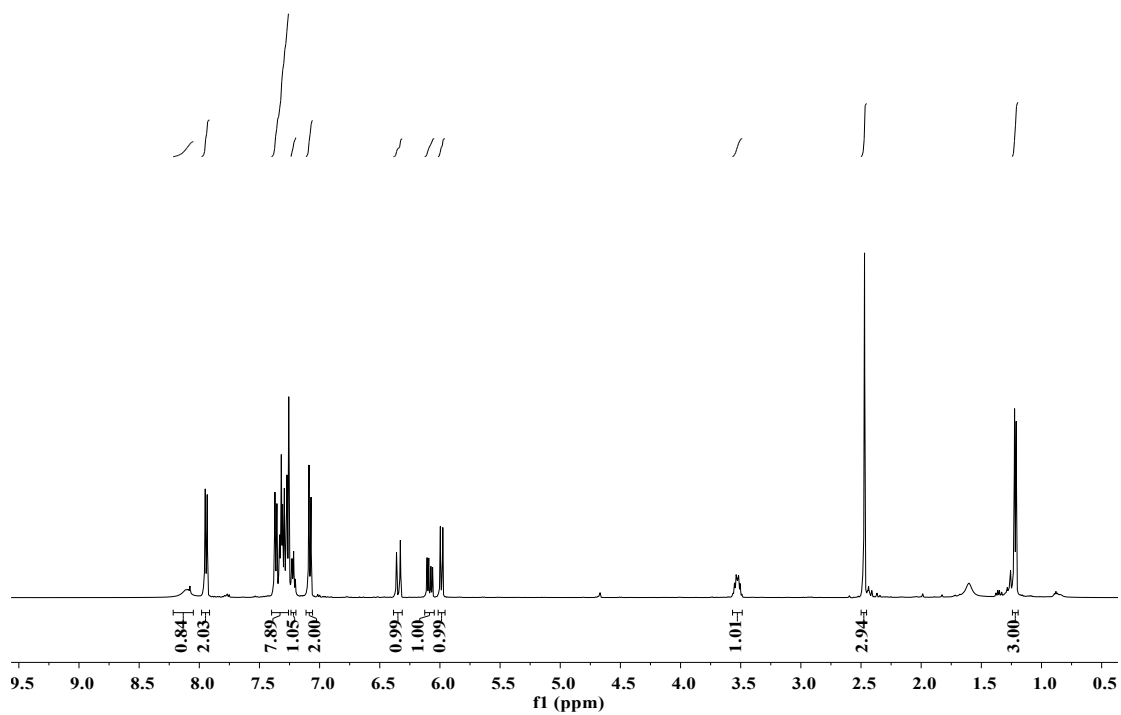
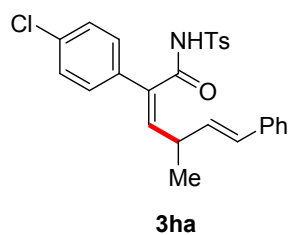
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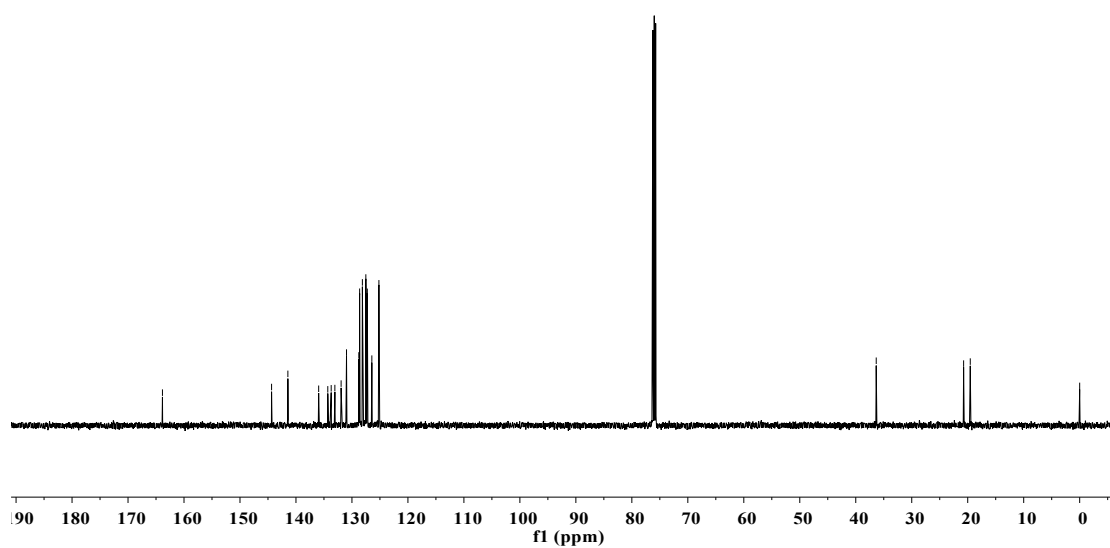
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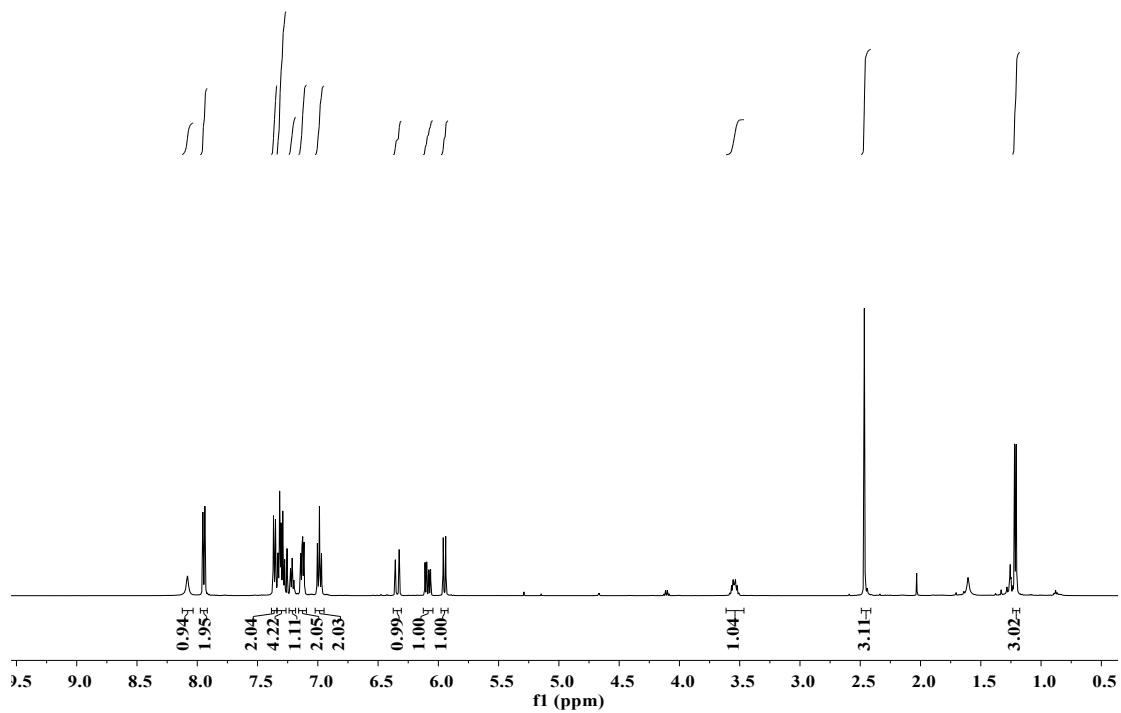
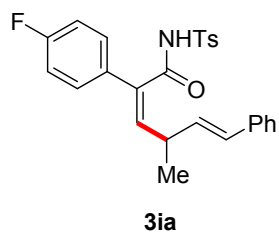




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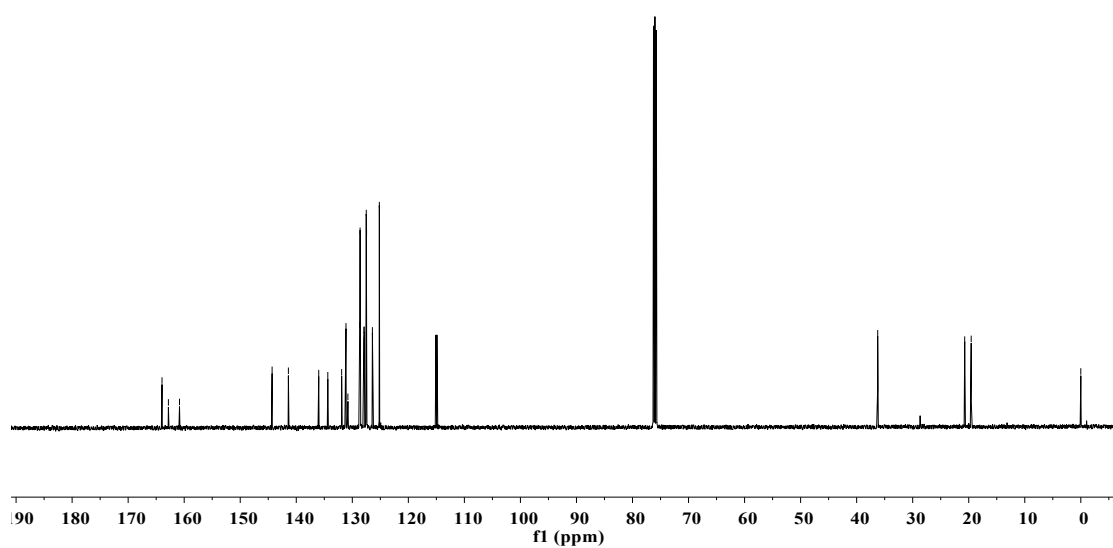
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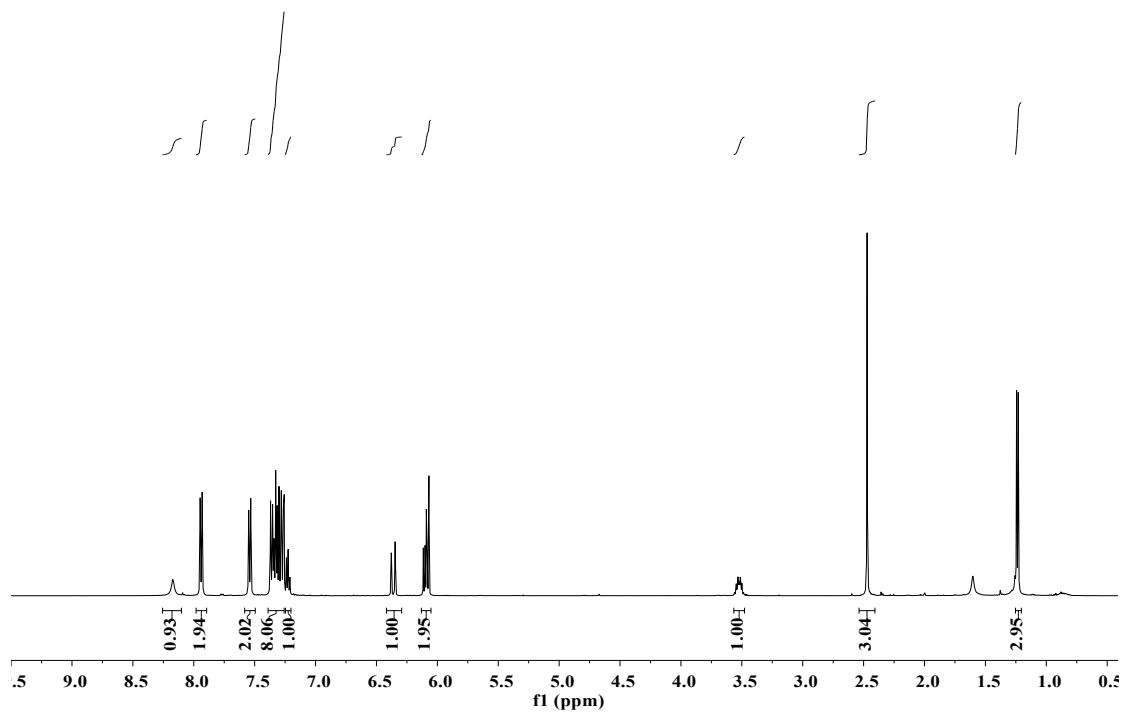
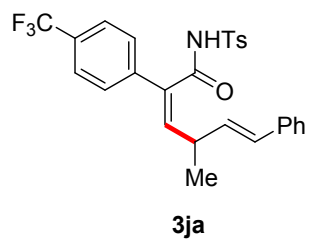




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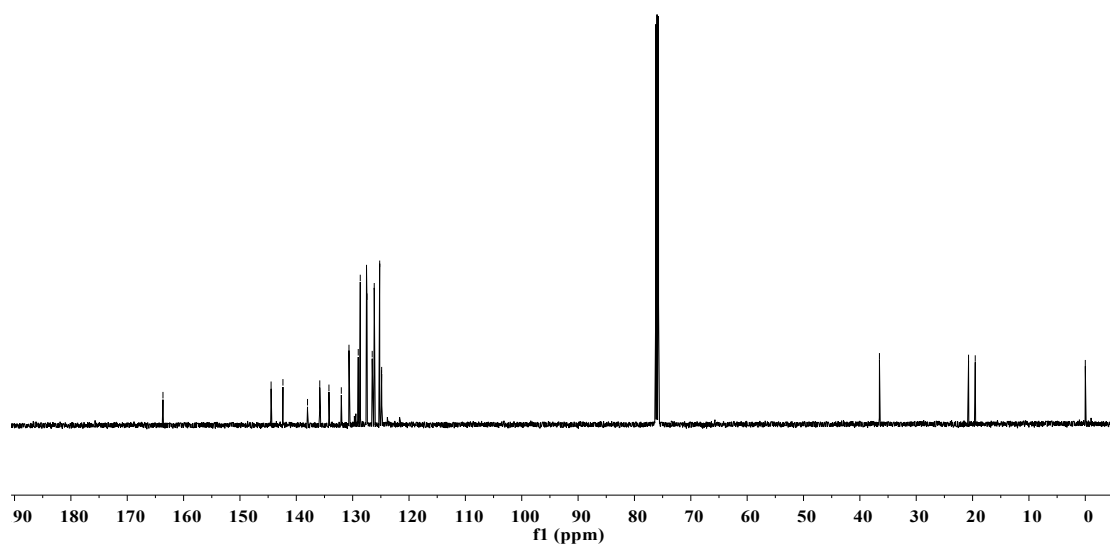


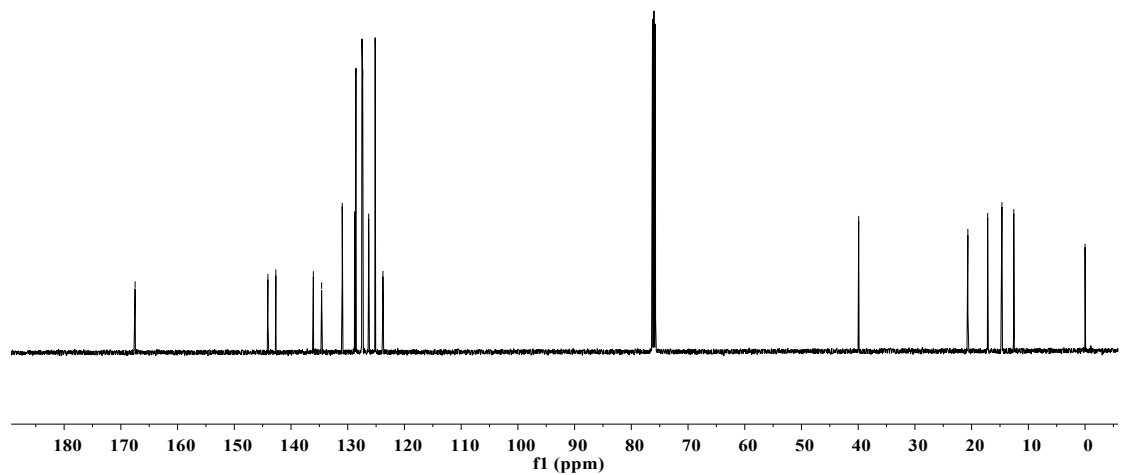
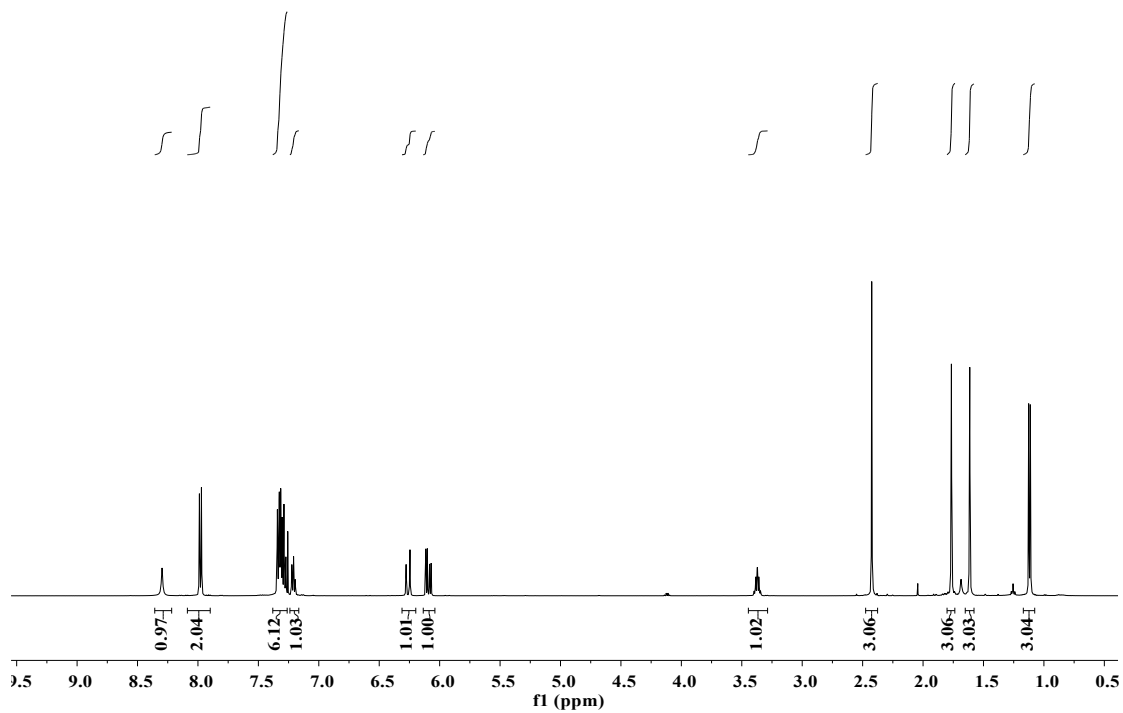
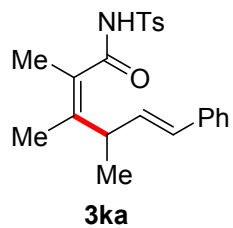
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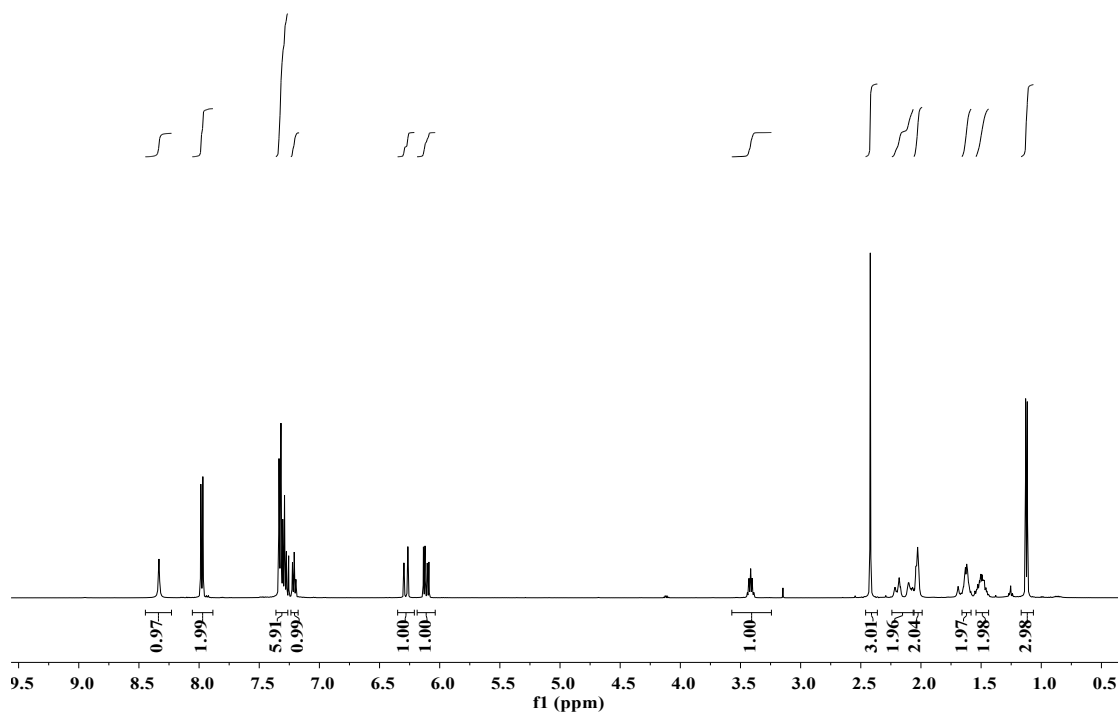
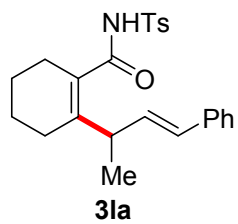
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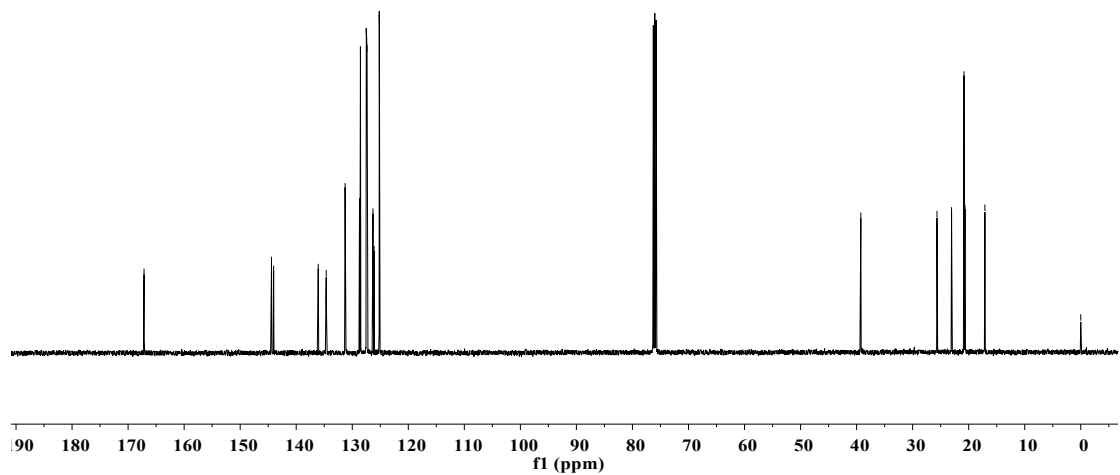


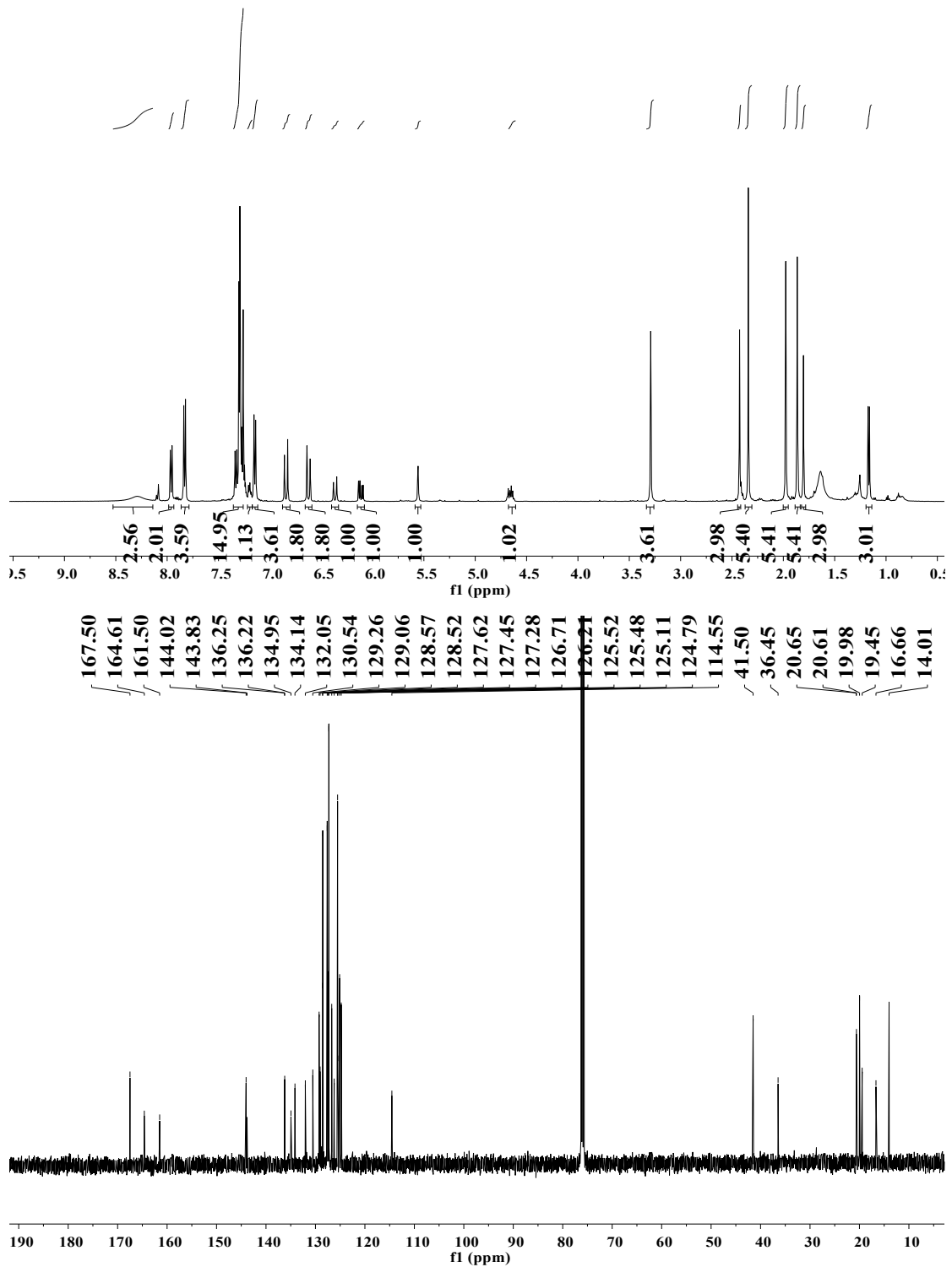
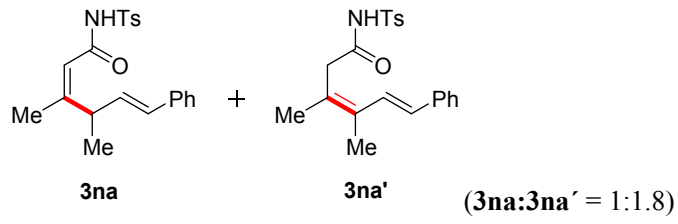


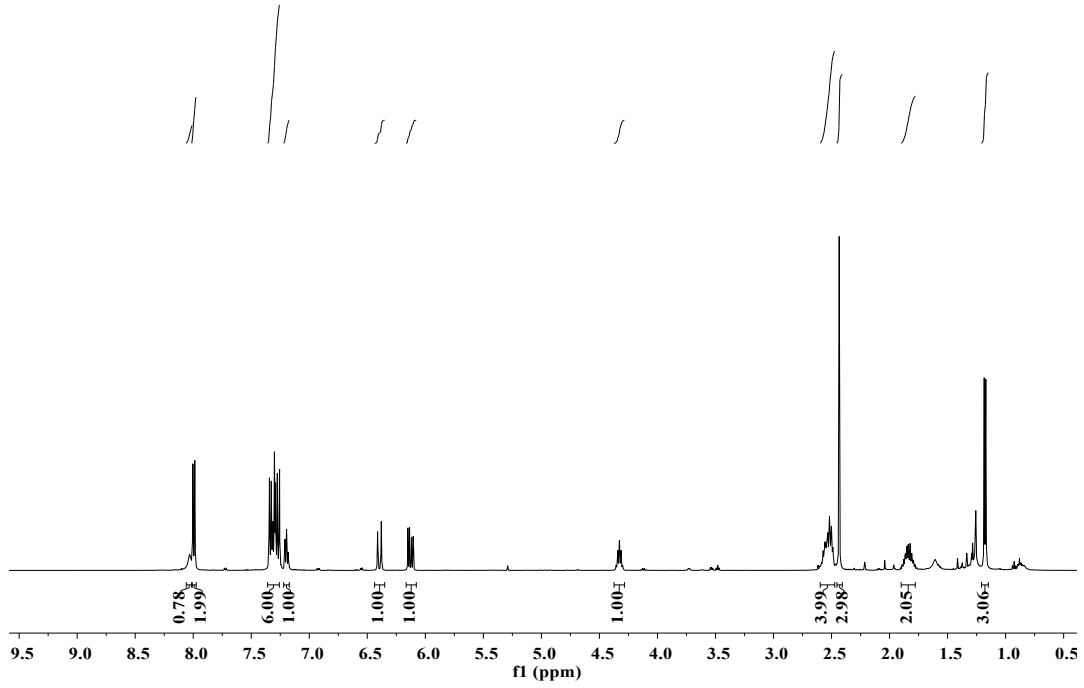
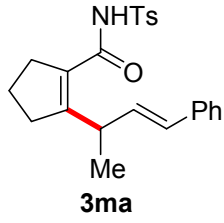


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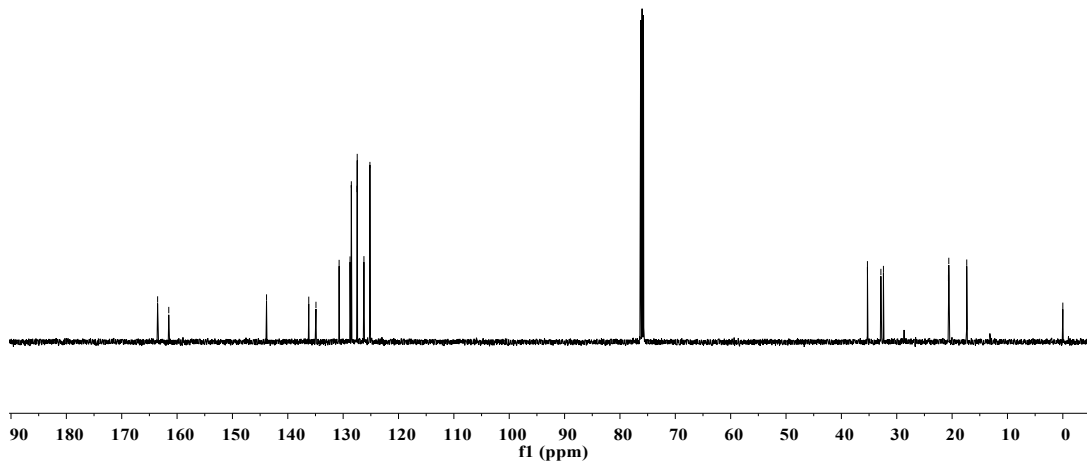


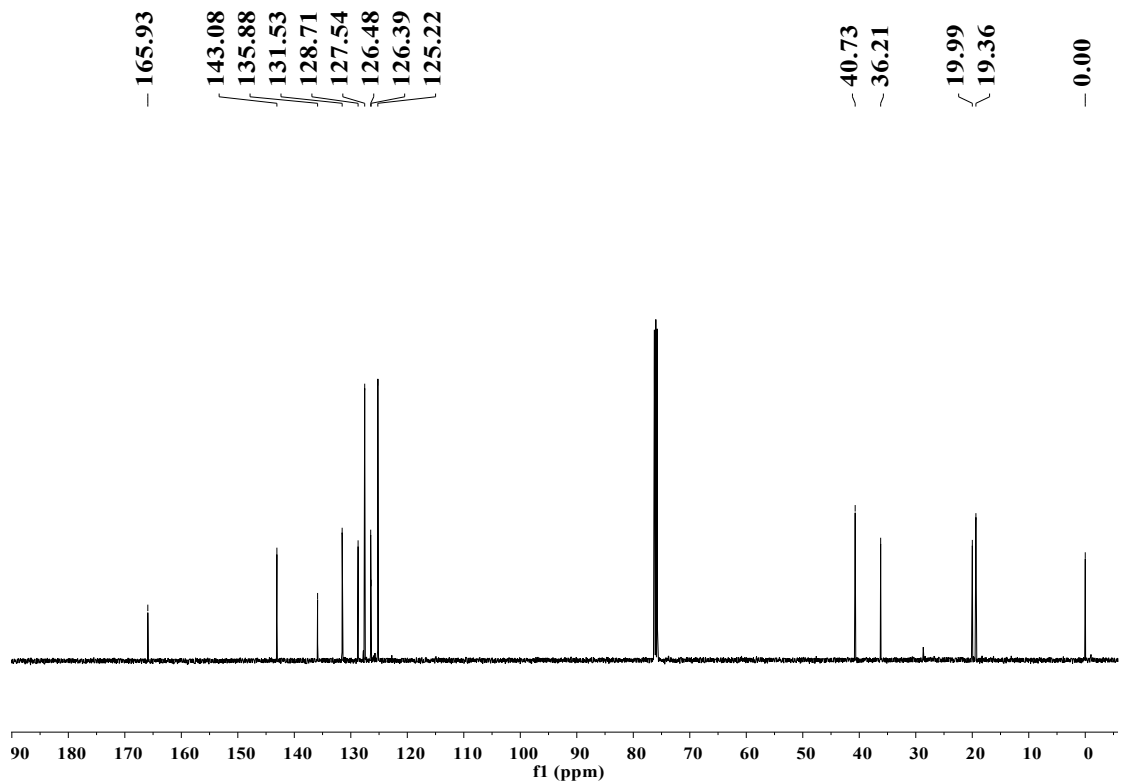
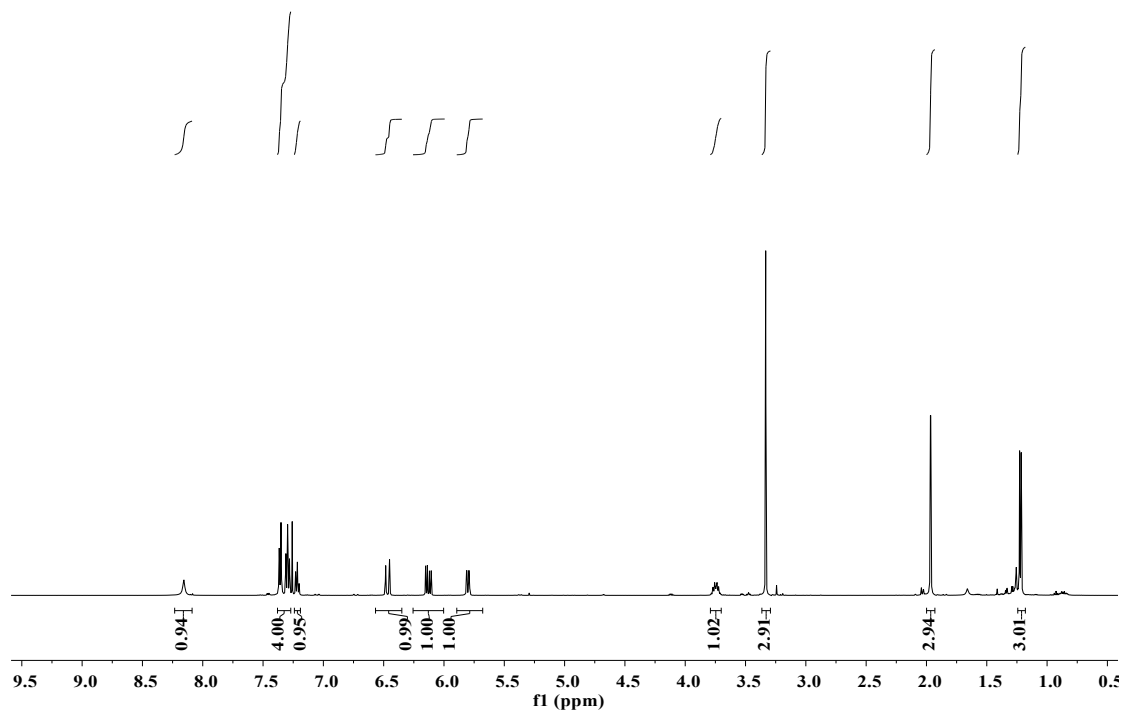
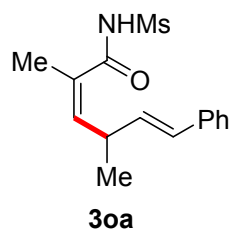


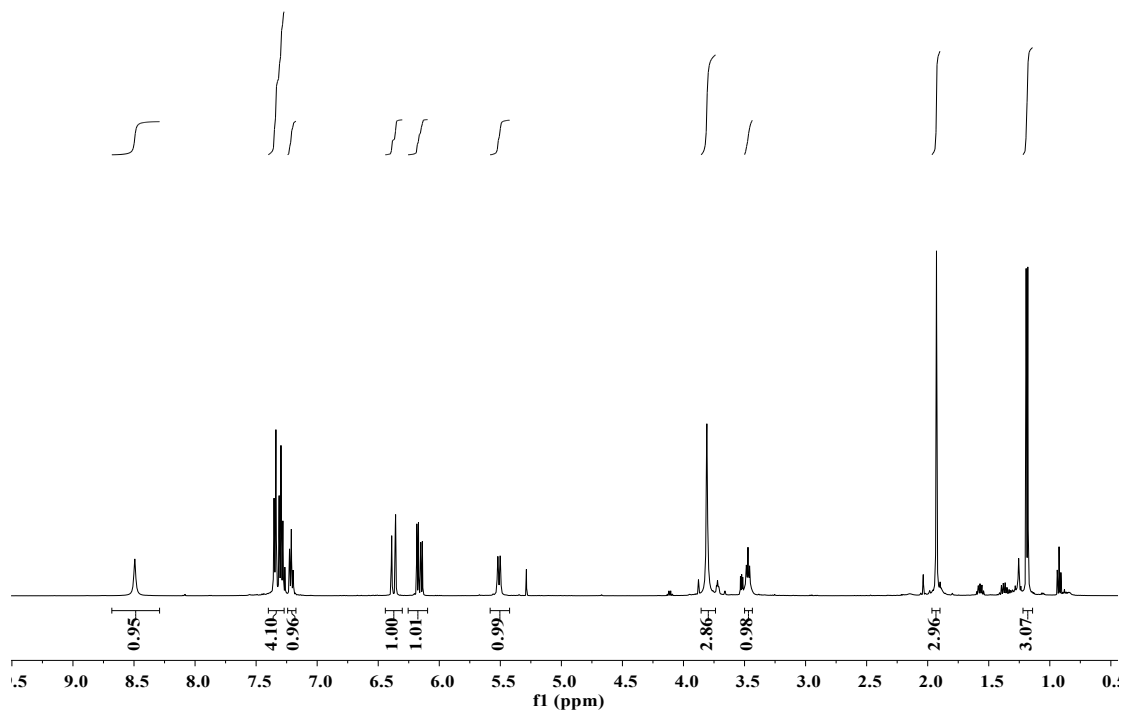
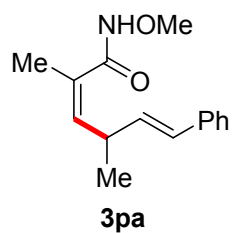
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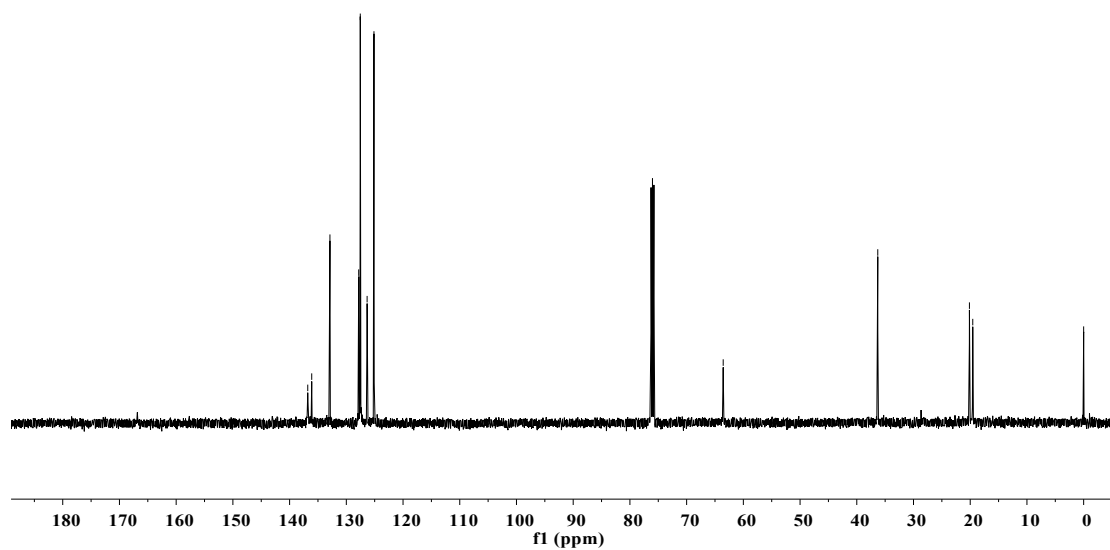
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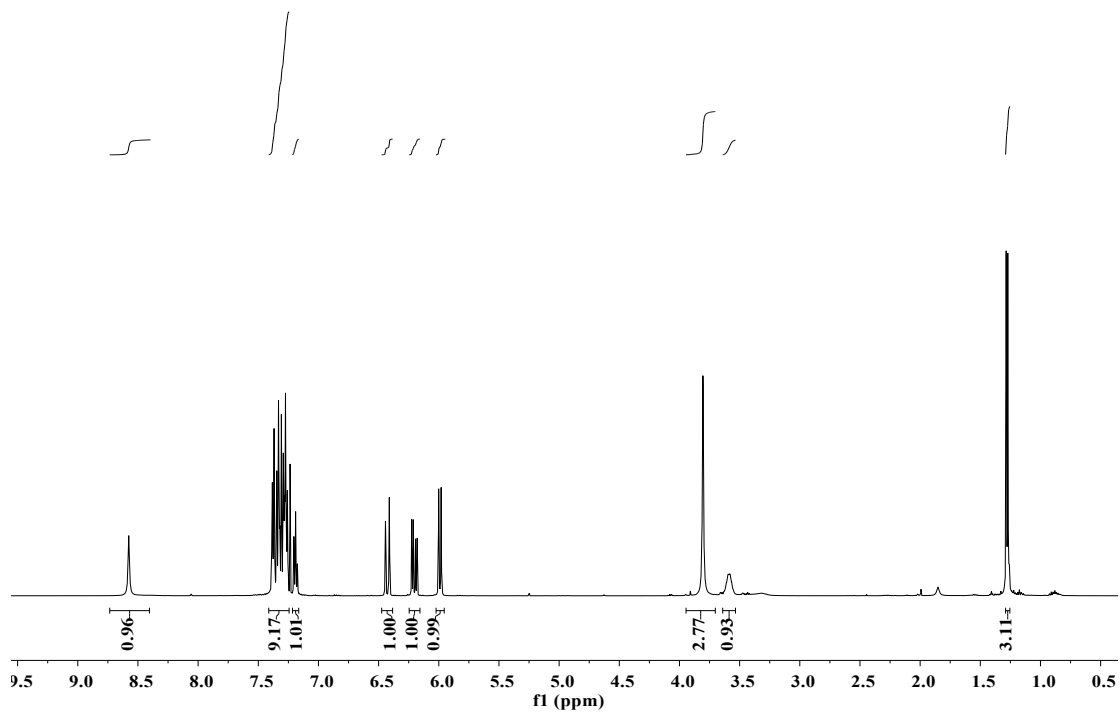
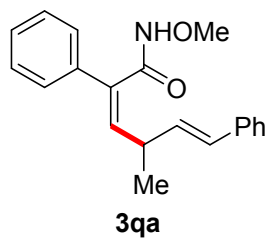






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 - 36.30
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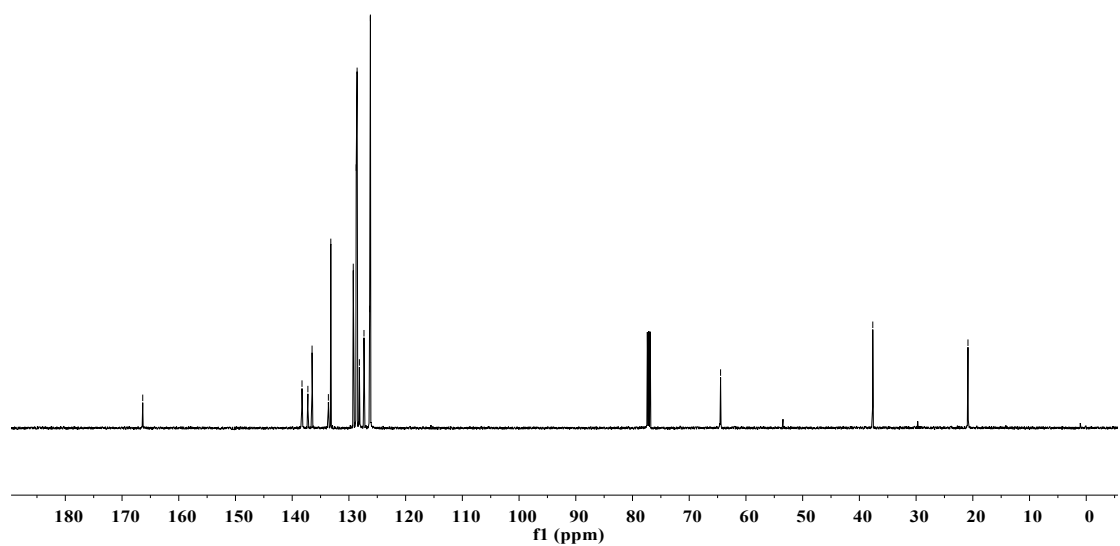


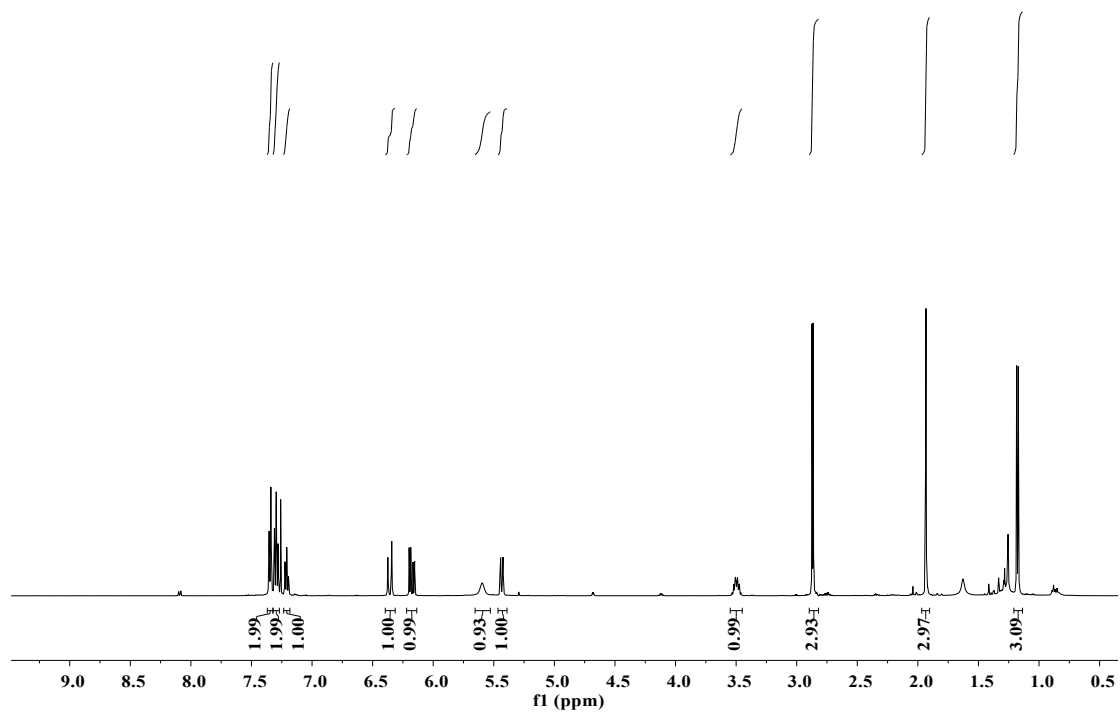
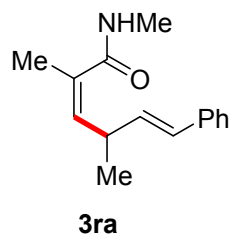
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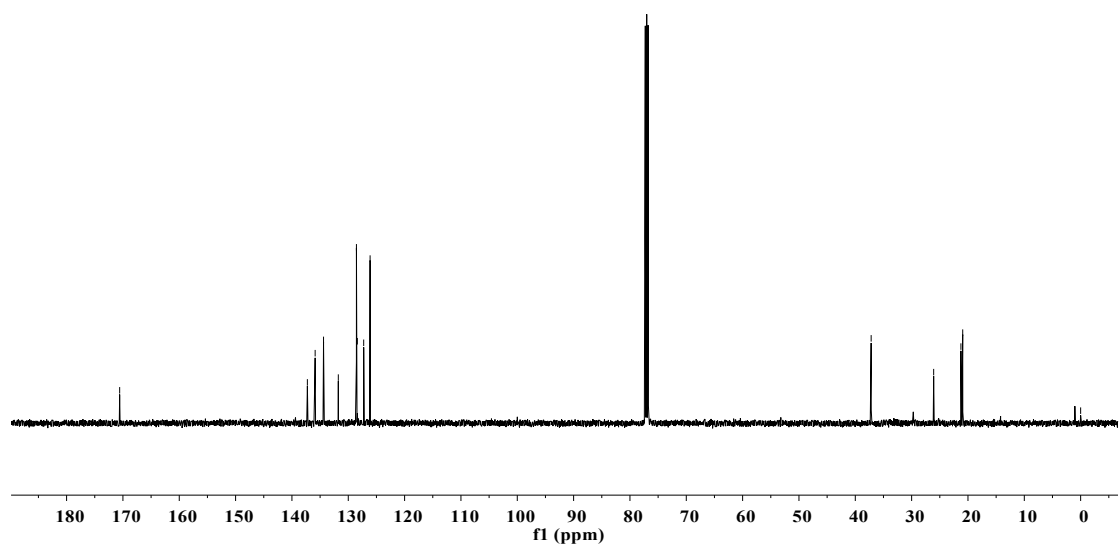
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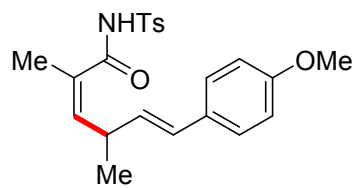
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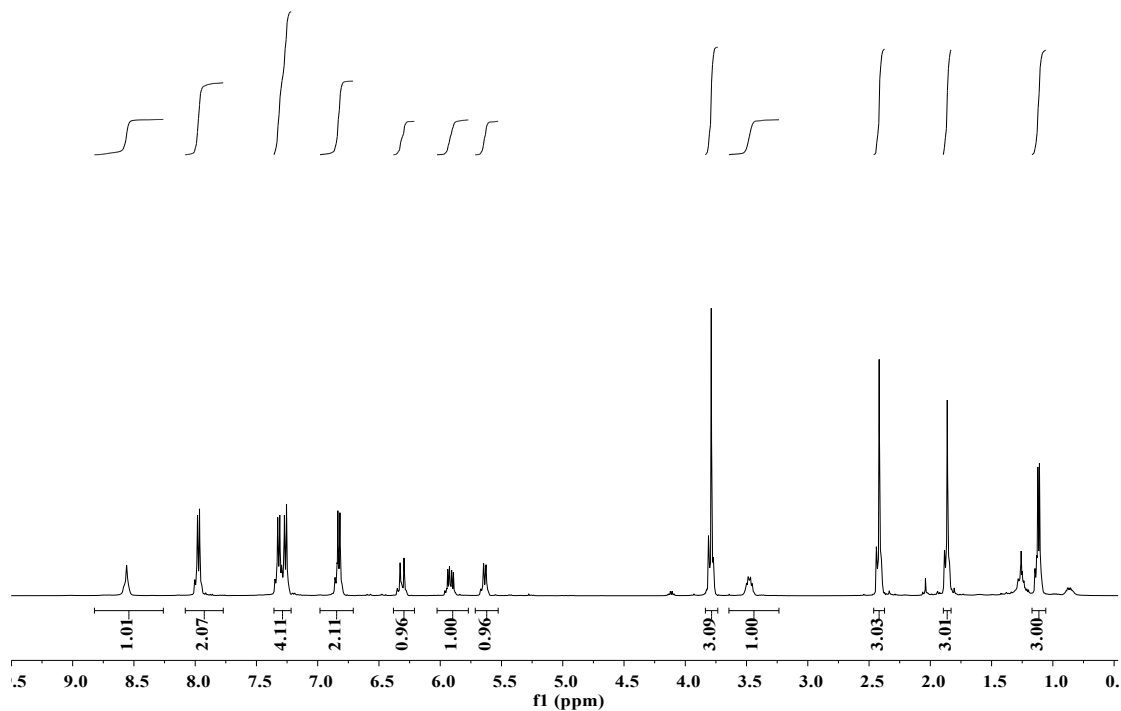


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3ac



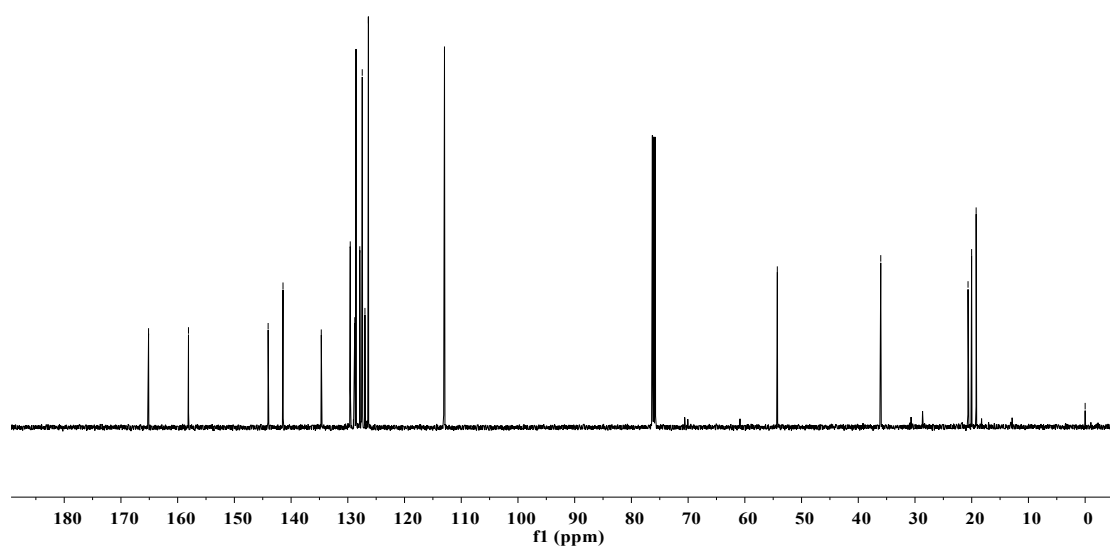
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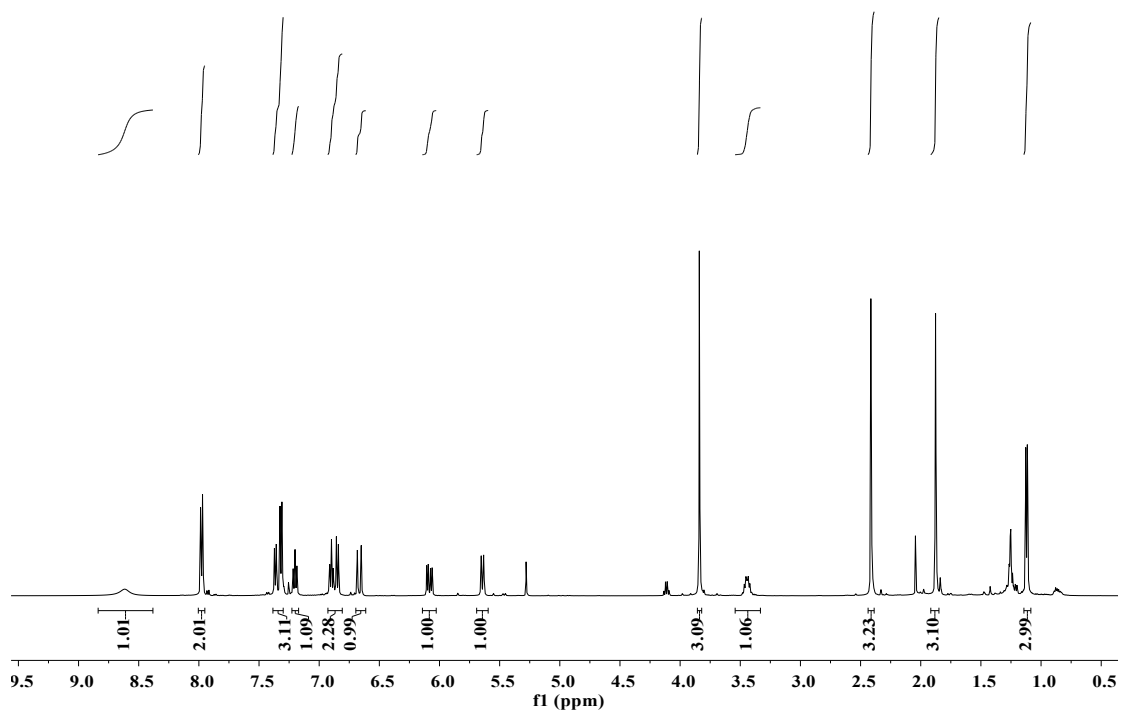
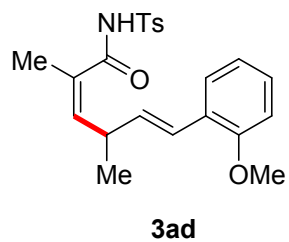
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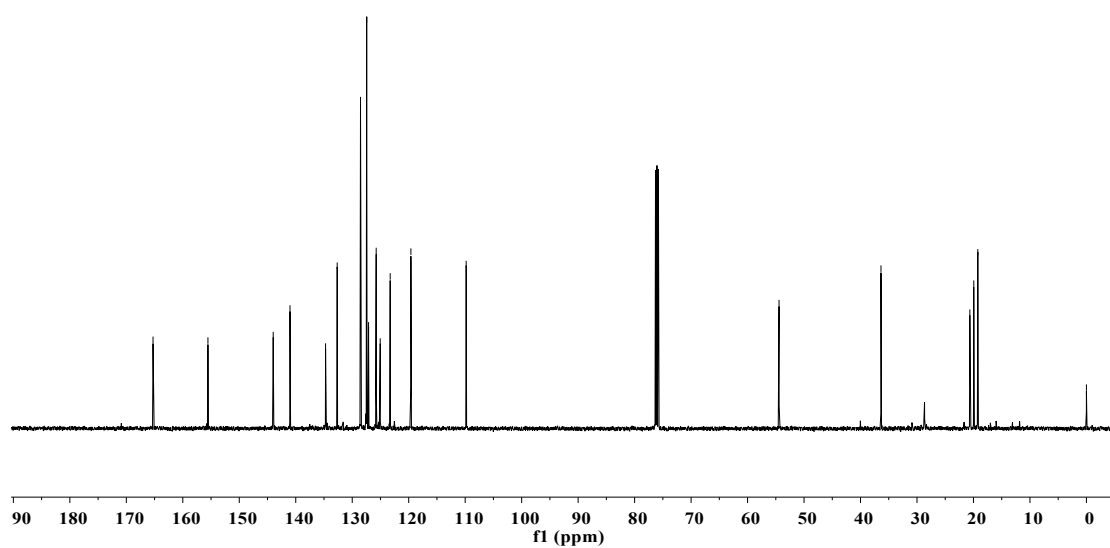
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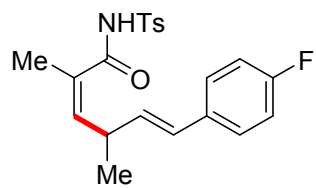
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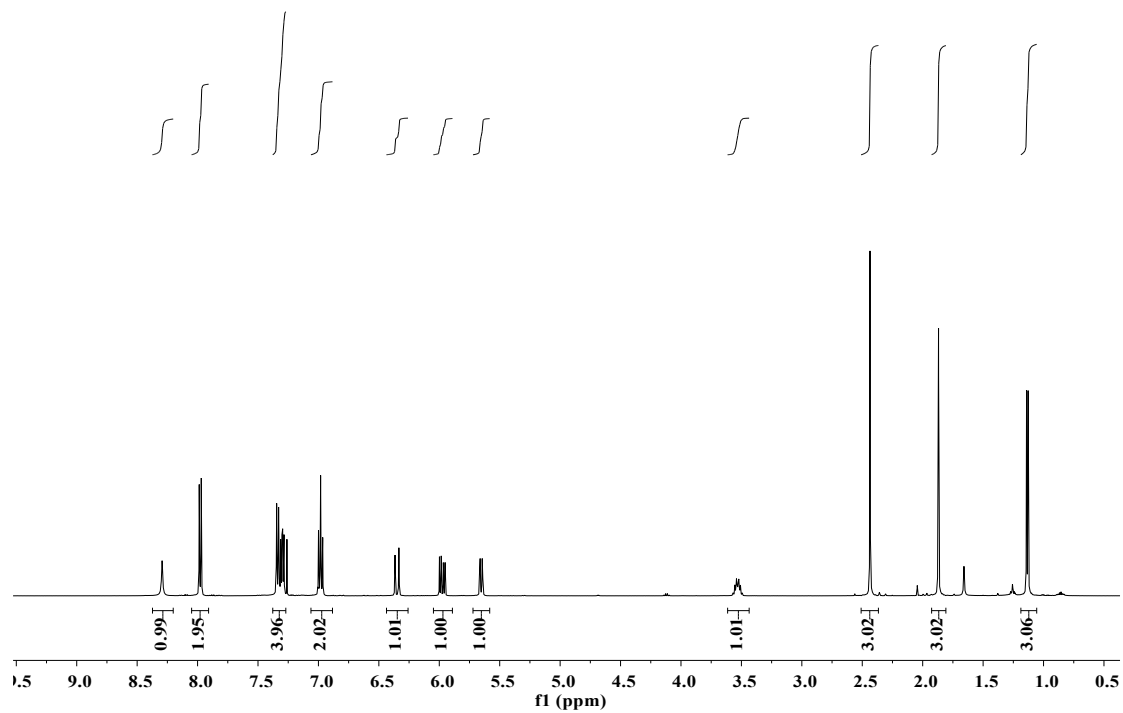


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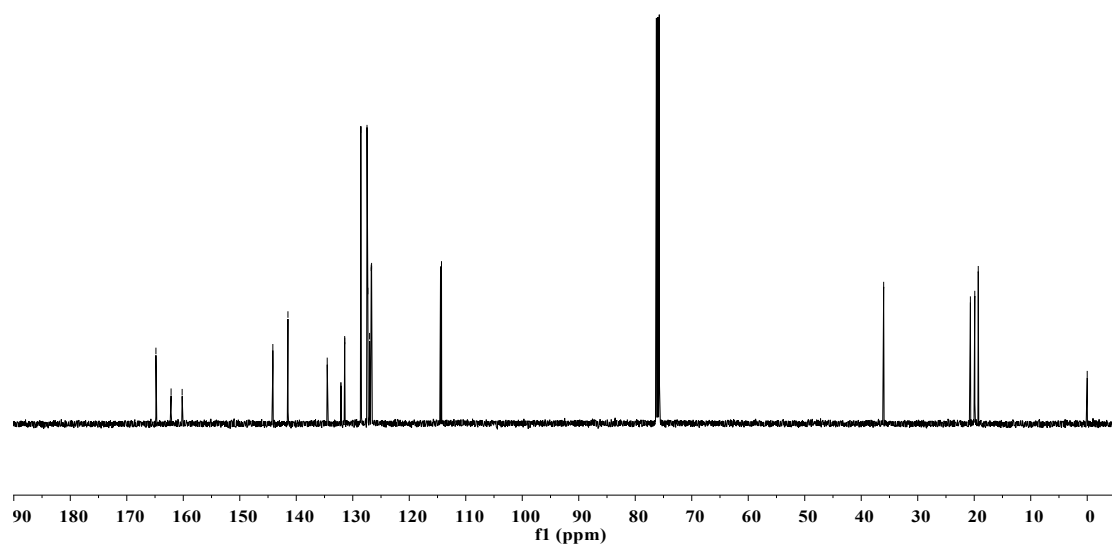


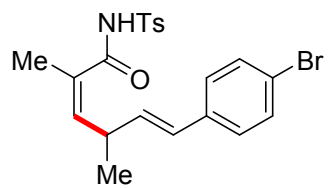


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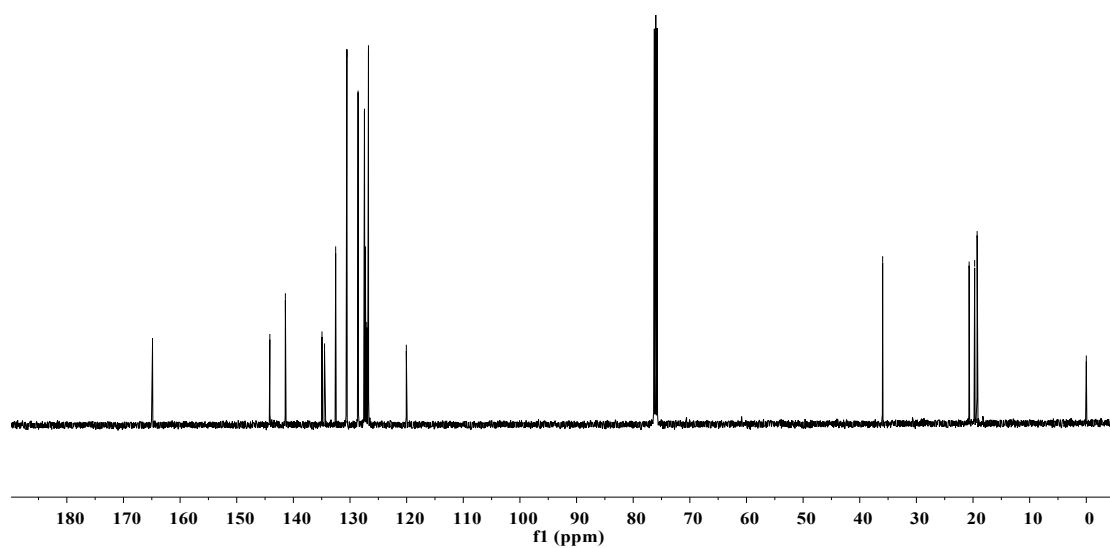
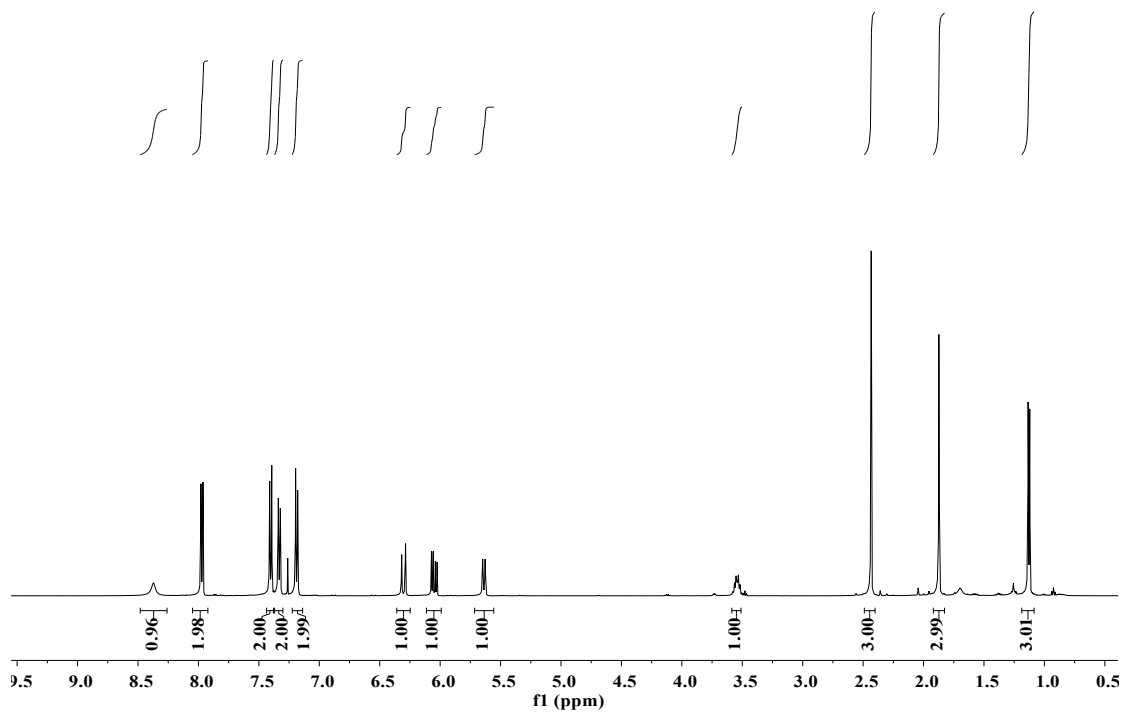


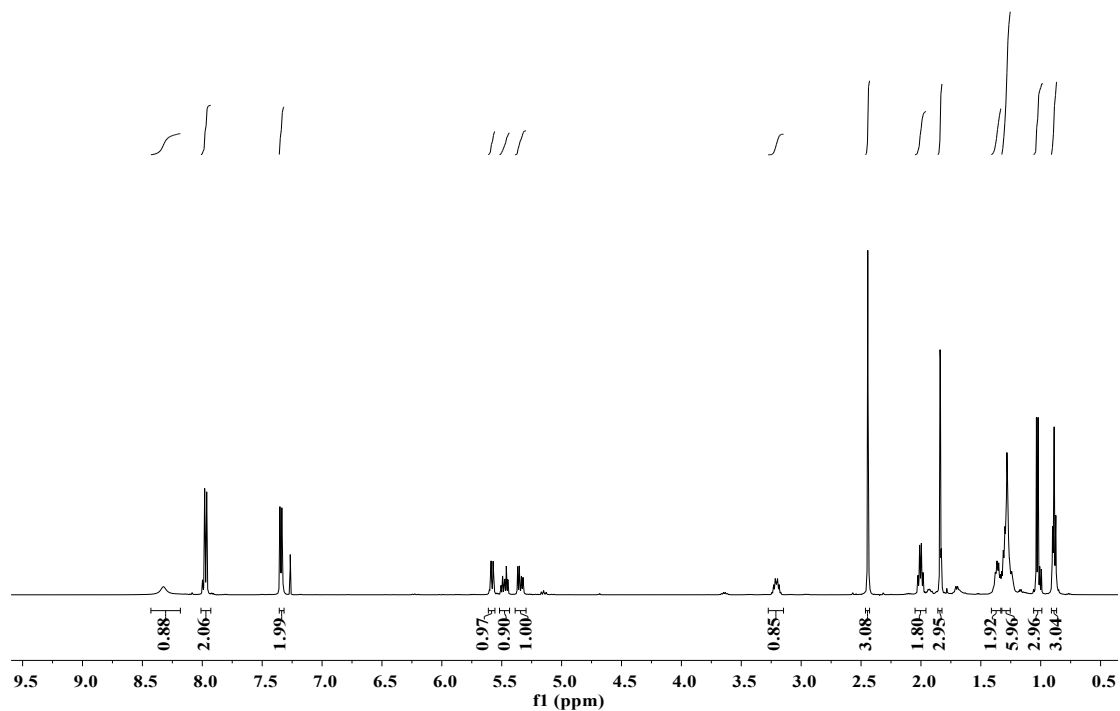
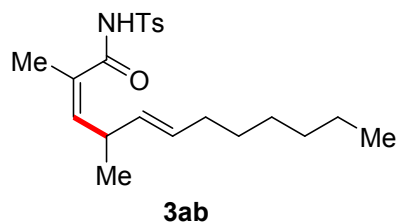
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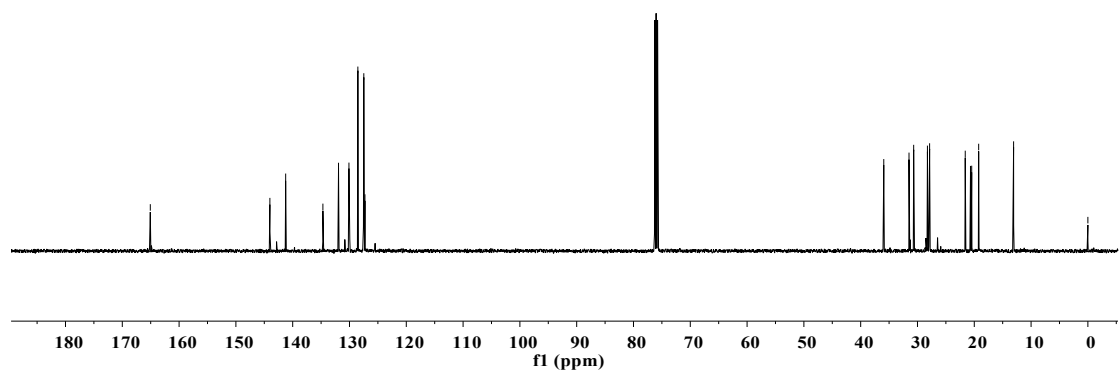
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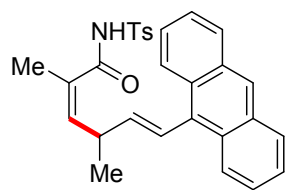




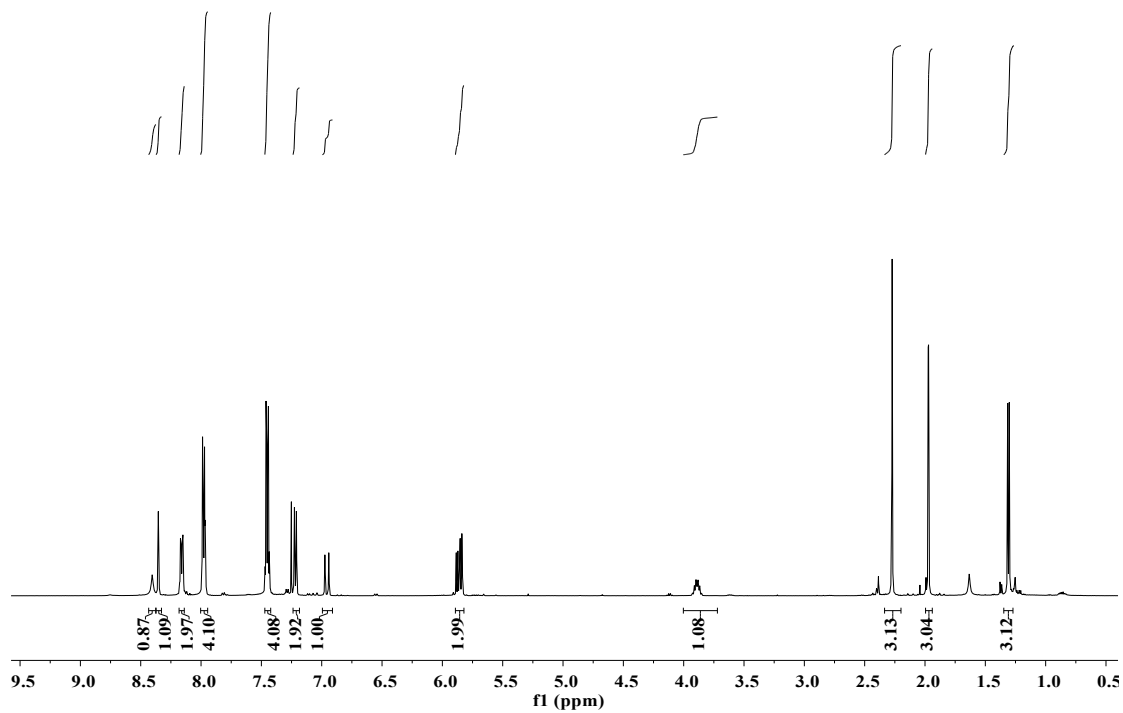
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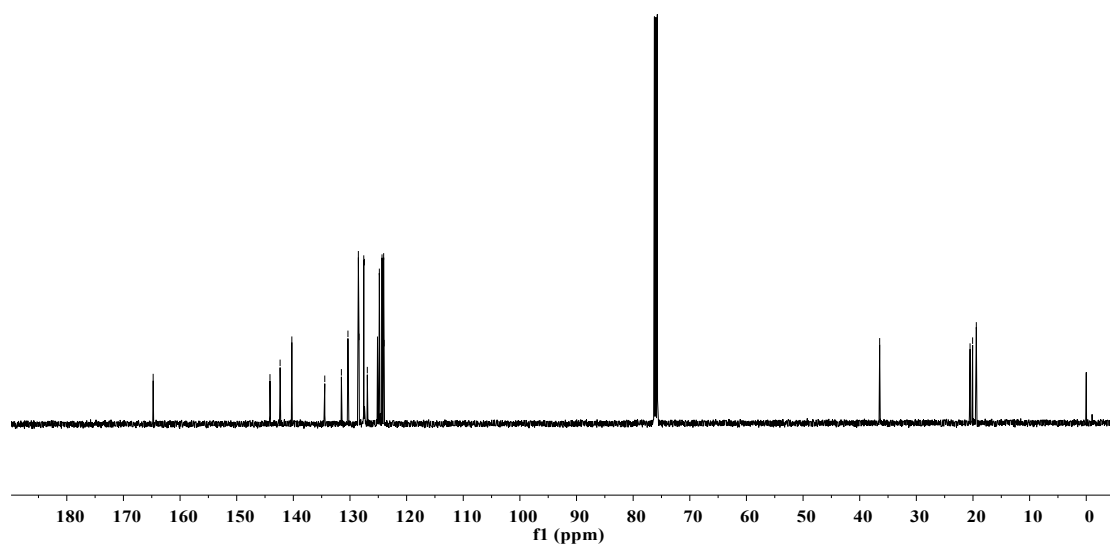


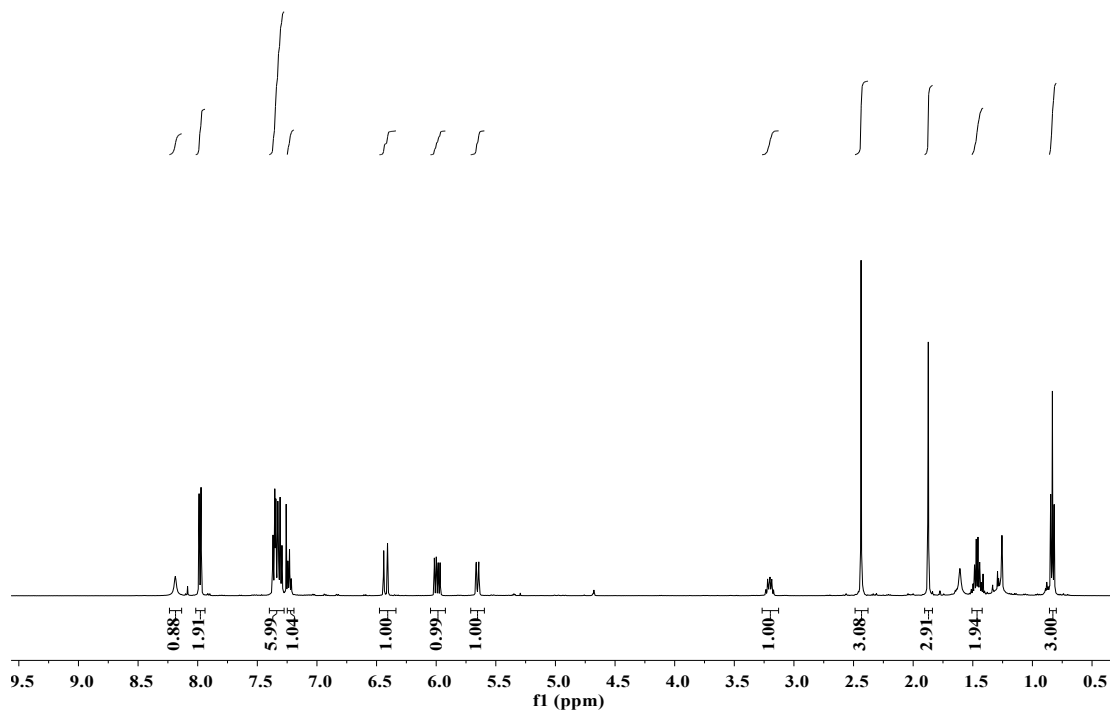
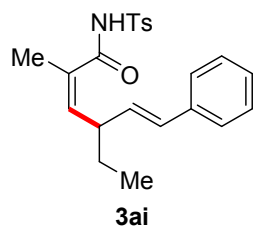
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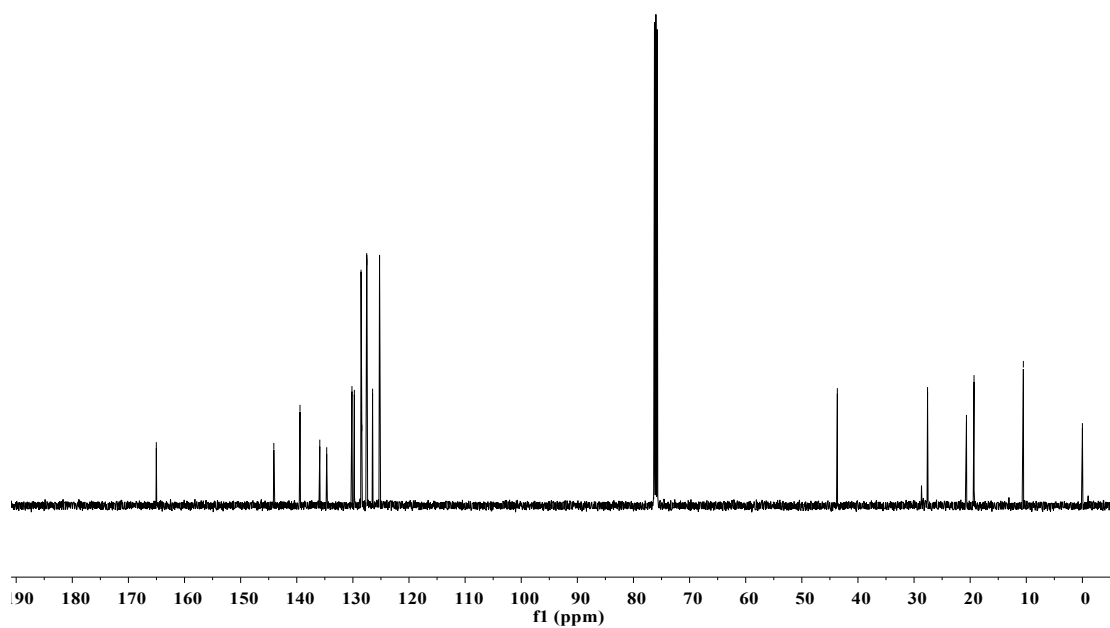
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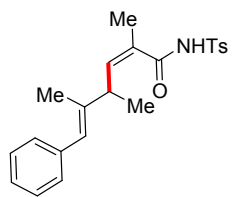
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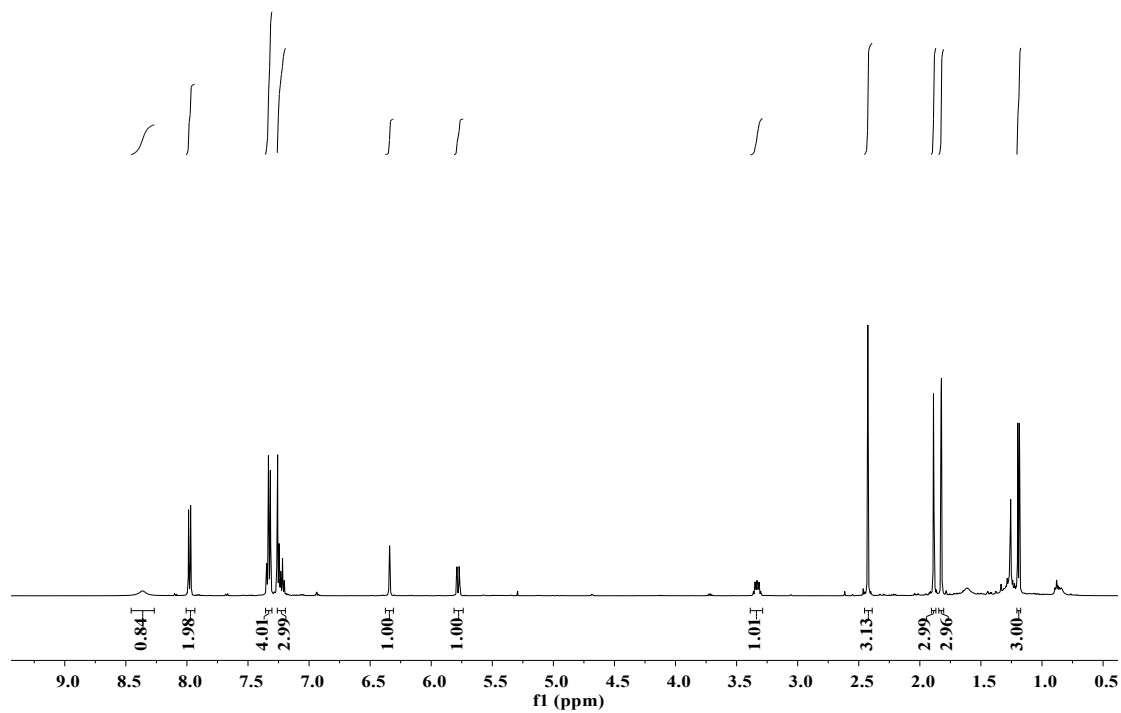


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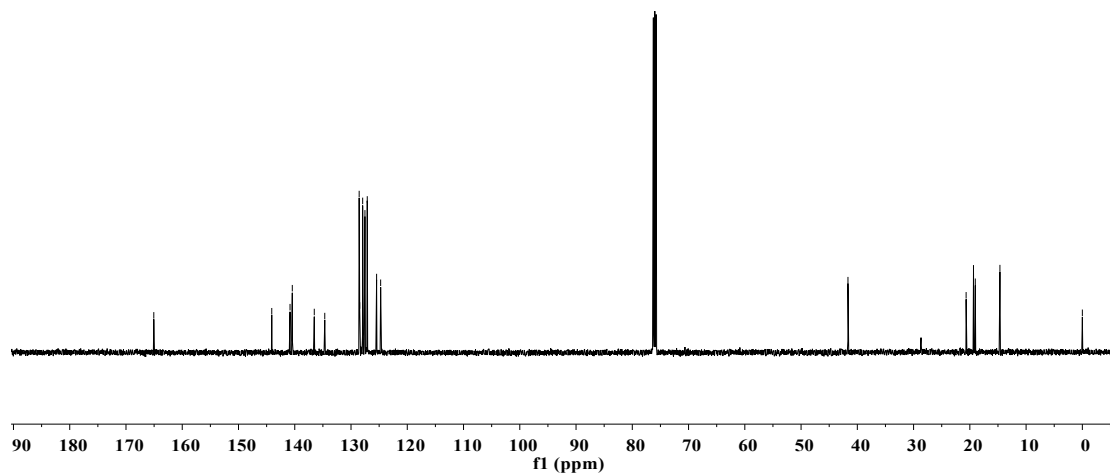


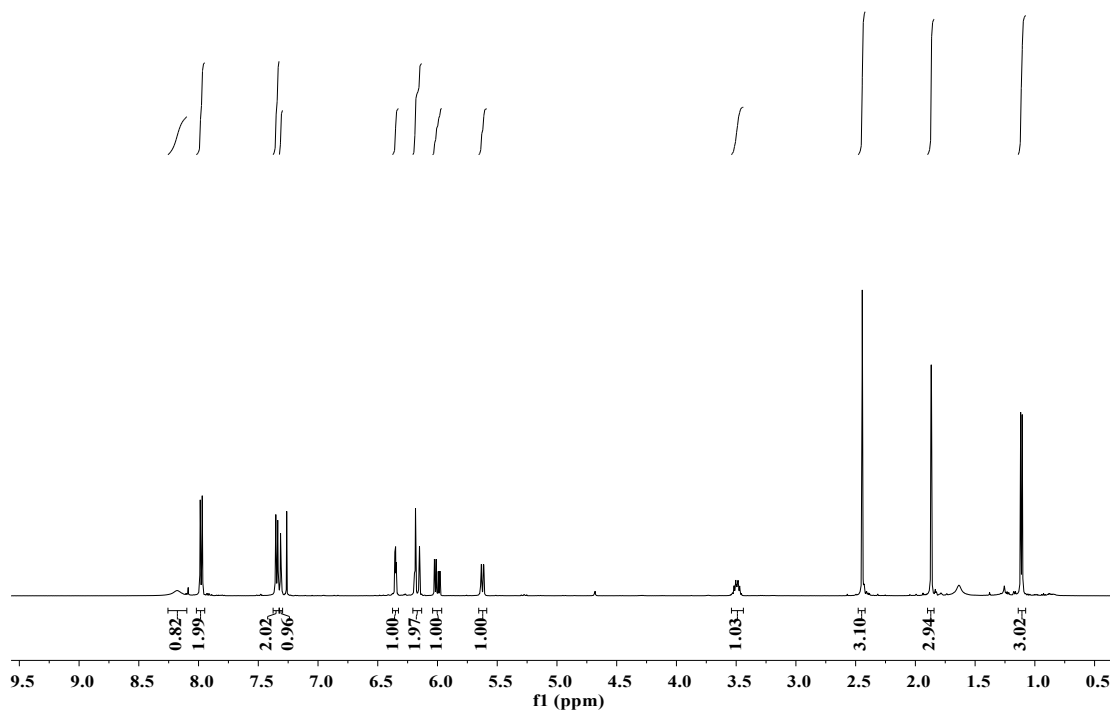
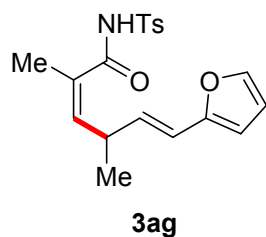


3aj



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164.80
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